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Silicone Rubber Passive Samplers for Water Quality Monitoring of Persistent Organic Pollutants in the Marine Environment

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CHAPTER 1: WATER QUALITY MONITORING OF PERSISTENT ORGANIC POLLUTANTS (POPS)

1.0 General Introduction

The marine environment can be subjected to the input of hazardous substances from a variety of sources, such as through atmospheric deposition, industrial and agricultural processes, sewage or industrial wastewater discharges, riverine inputs and poor environmental management (amongst others). A great number of these pollutants tend to be persistent in the environment [(1)] and are also often highly toxic to resident marine organisms and may ultimately be of concern to the consumer of marine produce. Additionally environmental monitoring requires sensitive analytical methodologies that allow for detection of persistent pollutants in marine biota and the water column itself.

Sampling and analysis of marine waters for a broad range of environmentally relevant persistent pollutants (e.g. polychlorinated biphenyls, and polyaromatic hydrocarbons) present significant analytical challenges, primarily as a result of low concentrations and incomplete phase separation between particle-bound and dissolved analytes [(2)]. Until recently regulatory monitoring of water has generally relied on the collection and analysis of "spot" samples for total or dissolved pollutant concentrations. Such discrete sampling approaches can often provide an unrepresentative picture of temporal (e.g. seasonal variation) and spatial charges (point source discharges).

Passive sampling (PS) is now internationally recognised as a promising technique in the area of contaminants analysis, where careful selection and deployment of appropriate passive sampling devices followed by targeted analysis can allow for the calculation of dissolved phase, time weighted, trace level water concentrations of a range of environmentally relevant pollutants. Interest in passive sampling techniques for marine and freshwater monitoring to support legislative requirements, to track pollutant fate and to aid in toxicological/bioaccumulation studies continues to grow.

This review presents information on current legislation with respect to monitoring of persistent organic pollutants (POPs) in the marine environment, describes the mechanisms by which contaminants may be accumulated in marine biota and discusses pollutants of interest within this project. Further review in Chapter Two reports the current "state of the art" of passive sampling methodologies encompassing quality assurance (QA), use of appropriate performance reference compounds (PRCs) to evaluate membrane sampling rates, the range of potential analytes and suitability for deployment in dynamic environments.

1.1 Legislative Frameworks for Marine Monitoring

It is widely acknowledged that chemical pollution can adversely affect aquatic environments. International legislation such as the Water Framework Directive [3], the Dangerous Substance Directive [4], the Shellfish Waters Directive [5], and the OSPAR (Oslo Paris Convention) joint assessment and monitoring programme (JAMP) [6] have all developed environmental spatial and/or temporal trend monitoring, for compliance with agreed quality standards or to complement integrated monitoring and assessments for a range of "priority" pollutants which are deemed to be toxic, stable and/or bioaccumulative. Frameworks relevant to marine monitoring are further described herein.

1.1.1 Oslo and Paris Conventions

In 1974, the Oslo Convention entered into force, primarily to regulate dumping operations involving industrial waste, dredged material and sewage sludge. The Paris Convention came into force in 1978, its principle aim being to prevent, reduce and, if necessary, eliminate pollution of the Convention area from land-based sources, which are discharged from rivers, pipelines, the coast, and also offshore installations and the

atmosphere [7]. The existing Oslo and Paris Conventions did not adequately control some of the many sources of pollution and the adverse effects of human activities upon it, taking into account the precautionary principle and strengthening regional cooperation [8]. This resulted in a merger of both commissions into the Convention for the Protection of the Marine Environment of the North-East Atlantic or OSPAR [9].

OSPAR established a Joint Assessment and Monitoring Programme (JAMP) whose main objectives include the preparation of environmental assessments of the status of the marine environment including the exploration of new and emerging problems in the marine environment [6]. The Coordinated Environmental Monitoring Programme (CEMP) Section of the JAMP describes a range of persistent substances to be monitored including polychlorinated biphenyls (PCBs) and polyaromatic hydrocarbons (PAHs). Ireland is a contracting party to OSPAR and is required to report annual environmental monitoring data to the ICES (International Council for the Exploration of the Sea) database on these pollutants. Current reporting practice revolves around the reporting of contaminant levels in suitable bio-monitor/bio-indicator species such as mussels. Such species act as a proxy for water contaminant levels as mussels being a filter-feeding species can accumulate pollutants in their tissues, with levels being representative of the environment in which the species reside.

1.1.2 Water Frame work Directive (WFD)

The WFD has been transposed into Irish Law by the European Communities (Water Policy) Regulations, 2003 [10]. The objectives of the WFD are to improve, protect and prevent further deterioration of water quality across Europe. The term ‘‘water’’ within WFD includes most types of water body – not only groundwater, but also surface waters (lakes, rivers, transitional and coastal waters) [11]. The Directive aims to achieve and

ensure good ecological and chemical status of all water bodies throughout Europe by 2015, and this is to be achieved by implementing management plans at the river basin level.

Monitoring is required to cover a number of quality elements including: [3]

1. **Physicochemical properties** (temperature, density, color, turbidity, pH value, redox potential, conductivity, surface tension, suspended solids, total/dissolved organic carbon);
2. **Hydromorphological status** (erosion and bench river characteristics);
3. **Biological** (distribution and composition of the species and biological effects);
4. **Chemical monitoring** (with particular emphasis on the contaminants in the list of priority pollutants).

The OSPAR priority pollutant list played an important role during the selection of priority substances for the WFD, with the final list resulting in 33 priority (groups of) substances [12]. The WFD has set out that a Member State shall implement the necessary measures to prevent deterioration of the status of all bodies of surface water, and shall protect, enhance and restore all bodies of surface water with the aim of achieving good status by 2015 [13].

The WFD does not prescribe the method by which individual countries report water quality data but direct analysis of spot water samples is currently favoured. The WFD does not specifically include PCBs on its list of priority pollutants, however their inclusion for mandatory OSPAR monitoring thus merited inclusion in this project. The potential pitfalls incorporated in such spot monitoring and the advantages of passive sampling techniques as completed in this thesis are further described in Chapter Two.

The WFD does not mandate any particular method of monitoring or chemical analysis, but requires that comparable methods, both of sampling and analysis, be used with good accuracy and precision so that differences between water bodies and trends can be detected reliably. A range of passive sampling techniques has already been developed and others are currently under development as support tools through EU initiative such as SWIFT-WFD (screening methods for water data information in support of the implementation of the water framework directive) and STAMPS (standardised aquatic monitoring of priority pollutants using passive sampling) [14, 15, 16].

1.1.3 Monitoring of Pollutants in Irish (coastal) Waters

Ireland is a contracting party to OSPAR and annually reports monitoring data (primarily in mussels) to the ICES database for use in Annual OSPAR assessments. Water quality in Ireland is also regulated by the European Communities (Water Policy) Regulations 2003 [10], which transposed the WFD into Irish law.

Under the WFD estuarine waters (transitional waters) monitoring is undertaken by the Environmental Protection Agency in collaboration with the Marine Institute, Central Fisheries Board and National Parks and Wildlife Service. In the new programme a total of 117 water bodies, consisting of 82 transitional (23 surveillance) and 35 coastal (12 surveillance), will be monitored [17]. Contaminants are measured in Irish coastal waters by direct spot water analysis (Shellfish Waters Directive) [5] and biotic flesh/liver analysis as previously described in the case of OSPAR reporting.

1.2 Persistent Organic Pollutants (POPs)

While many organic substances released to the marine environment are degraded rather effectively, the more persistent compounds may be distributed over large areas and may accumulate in organisms. Within OSPAR, attention is given not only to POPs but also to a range of hazardous substances based on a range of criteria such as bioaccumulation potential and toxicity. Bioaccumulation potential is primarily governed by a number of factors which are further discussed below.

The four general characteristics of persistent organic pollutants are that they are toxic, environmentally persistent, bioavailable to mammals and due to their semi-volatile nature; they are capable of travelling great distances [18]. Geyer et al [19] further describe the characteristics of POPs as having:

1. long range atmospheric transport potential,
2. sufficient volatility to evaporate and condense in air, water and soils at environmental temperatures,
3. a high persistence in soil, water and biota,
4. a very high lipophilicity (Log K_{ow} >5),
5. a high bioaccumulation potential,
6. potential toxic or adverse effects on reproduction, development and/or immunological function of aquatic and terrestrial organisms, including humans.
7. Many of these POPs have shown endocrine-disrupting effects, and some are carcinogenic in experimental animals.

The octan-1-ol–water partition co-efficient (K_{ow})

The K_{ow} is defined as the ratio of a compound's concentration in octanol to its concentration in water when the two phases are in equilibrium [20]. Thus, for a chemical A:

$$K_{ow} = [A]_{octanol}/[A]_{water} \qquad \textit{Eqn. 1.1}$$

Because the octanol phase mimics the solvation properties of lipids and biomembranes [21], K_{ow} is used as a measure of a compound's lipophilicity, which is associated with bioavailability, bioaccumulation, food-chain biomagnification, and toxicity [22, 23].

The values for K_{ow} are often expressed on a Log basis for the following reason: measured values of K_{ow} for organic chemicals range from 10^{-3} to 10^{7}, thus encompassing a range of ten orders of magnitude. In general terms, the Log K_{ow} thus will range from -3 to 7 for the majority of compounds [24]. The Log version is thus a more manageable figure.

The exact value of even very high K_{ow} values can be important. For example, the bioaccumulation potential of persistent organic chemicals in humans decreases sharply at Log K_{ow} values of between 9 and 11 [25]. One example of this is octachlorodibenzo-*p*-dioxin (OCDD) which has a Log K_{ow} of 8.6 [19].

Endocrine disrupters

Endocrine disrupters are chemical substances, from both natural and man made sources, that if present in the body at the right concentration and at the right time can adversely effect hormone balance or disrupt normal function in the organs that hormones regulate. These substances are often referred to as environmental estrogens.

According to the US EPA's working definition, endocrine disrupters "interfere with the synthesis, secretion, transport, binding, action, or elimination of natural hormones in the body that are responsible for the maintenance of homeostasis (normal cell metabolism), reproduction, development, and/or behaviour" [26].

Various authors [27-31] have reported endocrine disrupting chemical (EDC) mediated effects of organic compounds on aquatic life including, decreases in hatching success and in fertility of fish/shellfish, abnormal thyroid function in fish and species (de)feminization and (de)masculinization of fish and gastropods.

1.2.1 POPs of Interest in this Study

While there is a range of persistent organic pollutants, this thesis focuses solely on the analysis of PCBs and PAHs as they are included on the OSPAR Priority pollutant list (See Appendix 1[32]), and are recognized under other legislation as potentially harmful to the consumer. Summary information on the characteristics of these contaminant groups is discussed below and is detailed in Chapter Two.

1.2.1.1 Polychlorinated Biphenyls (PCBs)

Polychlorinated biphenyls or PCBs are a group of extremely stable aromatic chlorinated compounds which, like dioxins, are relatively resistant to biological degradation and hence persist and can accumulate in the environment and in the food chain. The production and use of PCBs has been discontinued in most countries, due to concern about their toxicity and persistence, but large amounts remain in electrical equipment, plastic products, buildings and the environment. Incorrect disposal of such material can result in continued release to the environment, adding to existing levels present as a consequence of past releases.

The so-called marker or indicator PCBs have been used as indicators of the total PCB content or body burden of environmental biota, food and human tissue. Wingfors et al [33] found the relatively persistent PCBs 56/60 and 66, the easily metabolized PCBs 44, 70 and 110 and the very persistent PCBs 153 and 180 were found to be good markers for occupational, recent occupational and background (dietary) exposure, respectively.

The most frequent approach is to use either the total level of six of the most commonly occurring PCBs (6 indicator PCBs, PCBs 28, 52, 101, 138, 153 and 180) or the total level of the seven ICES PCBs (7 indicator PCBs, PCBs 28, 52, 101, 118, 138, 153 and 180), including the dioxin-like PCB 118. The seven ICES PCBs were recommended by the European Union Community Bureau of Reference, selected as indicators due to their relatively high concentrations in technical mixtures and their wide chlorination range (3–7 chlorine atoms per molecule) [34]. These seven congeners are generally considered to be stable in the environment and may be good markers for human PCB exposure through food [33].

The European Food Safety Authority (EFSA) report that technical PCB mixtures used in toxicity studies exert a variety of toxicological effects such as effects on liver, thyroid, immune function, reproduction and behaviour as well as carcinogenicity. The adverse effects reported in laboratory animals following exposure to individual non dioxin-like PCBs were effects on the thyroid, liver and brain biochemistry, as well as immunotoxicity, oestrogenicity, and reproductive and neurodevelopmental effects [35].

1.2.1.2 Polyaromatic Hydrocarbons (PAHs)

Polyaromatic hydrocarbons (PAHs) are widespread chemical pollutants that can be introduced into the environment via a number of sources including: incomplete combustion at high temperatures (pyrolytic origin), slow degradation of organic matter to form oils and related products (petrogenic origin), short term diagenetic degradation of biogenic precursors (diagenesis) and direct biosynthesis by organisms (biogenic PAHs) [36]. The majority of environmental inputs are however linked with anthropogenic activity.

The United States Environmental Protection Agency (US EPA) has identified 16 PAH as priority pollutants. Some of these PAH (eight of the sixteen [37]) are considered to be possible or probable human carcinogens and hence their distribution in the environment, and their potential exposure to humans, has been the focus of much attention in relation to consumer safety and human health [38].

1.3 Pollutant Bioconcentration, Bioaccumulation and Biomagnification

PCBs and PAHs are often both persistent and soluble in fats (lipophilic) and therefore capable of accumulating in the fatty tissues of aquatic animals. Fat soluble pollutants can build up to concentrations thousands of times higher than in the surrounding water.

Lipophilic organic contaminants or their metabolites may accumulate at high levels in animal tissues and interfere with normal metabolic processes that affect growth, development, and reproduction [39]. The toxic effects of chemical contaminants on marine organisms depend on the bioavailability and the persistence of these contaminants, the ability of organisms to accumulate and to metabolize them, and their interference with specific metabolic and ecological processes [40, 41] Accumulation of contaminants in biological resources may occur through aqueous, sedimentary or dietary pathways [41].

Accumulation of pollutants can occur through a variety of mechanisms including pollutant bioconcentration, bioaccumulation and biomagnification. Principles underlying pollutant uptake and factors influencing these mechanisms in marine animals are further described below.

1.3.1 Bioconcentration

Bioconcentration occurs as a result of the direct uptake of a chemical by an organism from the water phase [19]. Although concentrations of POPs dissolved in water are usually less than 1 part per billion, organisms often bioconcentrate these low levels of contaminants in water to relatively high levels in their tissues [42]. Thus determination of

the dissolved portion of environmental pollutants (as occurs using passive sampling techniques) is critical for assessing the potential for detrimental biological impacts.

The result of bioconcentration is generally expressed in terms of an experimentally derived **bioconcentration factor (BCF)** [19]. *Eqn. 1.2* depicts the BCF as the ratio of the steady state concentration of a chemical in an aquatic organism (C_F) to the corresponding freely dissolved chemical concentration in the surrounding water column (C_w).

$$BCF = \frac{C_F}{C_W}\frac{[ng/kg^{-1}]}{[ng/L^{-1}]} = \frac{K_1}{K_2} \qquad \textbf{Eqn. 1.2}$$

Where:

C_F and C_w relate to the steady state of the chemical in the organism and the concentration in the water.

K_1 and K_2 relate to the uptake, clearance and release rate constant.

1.3.1.1 Factors Affecting Bioconcentration

The passive bioconcentration of a chemical by an aquatic organism depends on various abiotic factors, including the physical and chemical properties of the chemical in question, water solubility rates (Log K_{ow}), the temperature and flow rates of the water body, as well as biotic factors such as species, sex, health status, growth rate and compound elimination rates and /or the half life of the chemical in the test species [19].

1.3.1.1.1 Physco-Chemical Properties

The BCF is dependent on physico-chemical properties such as the molecular weight, water solubility and lipophilicity of a chemical. The higher the Log K_{ow} value of a non-metabolised chemical, the greater the potential for bioconcentration in an aquatic organism [19].

1.3.1.1.2 Bioavailability

Contaminant accumulation in biological tissue requires the compound to be present at the animal–environment interface in the dissolved state, therefore only the truly dissolved fraction of a chemical is bioavailable. Burkhard [43] reports that the bioavailability, fate, and behavior of hydrophobic POPs in aquatic ecosystems are directly influenced by the dissolved and particulate organic carbon present. Golding et al [44] contended that fugacity can act as a useful measure of the bioavailability of sediment-associated POPs. In this context, a low fugacity would indicate that the chemical was sorbed tightly to the sediment particle and would be less available for desorption into the pore-water phase from which it could be readily bioaccumulated. Processes which may influence/reduce the bioavailability of hydrophobic chemicals include; binding to particulates and dissolved organic matter, and adsorption to humic acids, sediments and other suspended materials [19]. The formation of colloidal suspensions can also reduce bioavailability.

1.3.1.1.3 Role of Lipids in Bioconcentration

The lipid content of organisms is of crucial significance for the amount of fat soluble toxic pollutants they contain [19]. Fish and marine invertebrates can take up such substances directly from the water through their gills, skin or similar organs (bioconcentration), and can potentially rid themselves of an excess of the pollutants in the same way. Thus concentrations of fat-soluble pollutants in marine biota are normally more or less in equilibrium with the concentrations to be found in the surrounding water [45].

In general, the greater the lipid content of the aquatic organism, the greater the bioconcentration potential of the chemical [19].

$$BCF_L = \frac{BCF_W * 100}{L_W(\%)} \qquad \textbf{Eqn. 1.3}$$

Where:

BCF_L and BCF_W represent the bioconcentration factor (BCF) on a lipid and wet weight basis respectively.

$L_W(\%)$ = Percentage lipid in the organism on a wet weight basis.

The following equation (as further examined in Section 4.7.1.1) can be used for the prediction of BCF_L values of relatively persistent organic chemical in mussels if their lipid content is known:

$$\text{Log } BCF_L = 0.956 \text{ Log } K_{ow} + 0.22 \qquad \textbf{Eqn. 1.4} \ ^{(19)}$$

1.3.2 Bioaccumulation of Contaminants in Food Webs

Bioaccumulation has been described as the uptake and retention of a bioavailable chemical from any one of, or all possible sources, it being the net result of uptake, distribution and elimination of a substance in an organism due to water, food, sediment and air [(46)]. In bioaccumulation a number of additional biological, temporal and trophic factors have to be further considered. The rate of uptake of a chemical must be greater than the rate of metabolism/elimination of the compound within an organism in order for bioaccumulation to take place. Bioavailable chemicals whose physico-chemical properties subject them to potential bioaccumulation will passively diffuse or will be transported across the outer membranes of an organism down a concentration or activity gradient [(47)]. Following ongoing exposure a steady state situation may be reached where the chemical concentration in the tissue reaches equilibrium with the outside medium [(48)]. The equilibrium concentration is generally measured as the bioaccumulation factor (BAF), i.e. the ratio of the concentration of the chemical in the tissue to its concentration in environmental compartments.

1.3.3 Biomagnification of Chemical Pollutants

Marine organisms are able to bioaccumulate organic contaminants from their food, this process being often referred to as trophic transfer. Biomagnification is the process whereby a chemical, as it is passed through a food chain or food web by trophic transfer, increases in concentration in each subsequent trophic level. Contaminants present in the prey of the consumer may be desorbed and dissolved during digestion processes where subsequent partitioning processes across the gut epithelia take place into tissues of the consumer. Where the efficiency of uptake is relatively high and the rate of elimination/metabolism is relatively low, contaminant levels may then increase, thereby biomagnify, through the marine food web by trophic transfer.

For organic compounds with a Log K_{ow} >6 water solubility is low, partitioning from lipids to the aqueous phase across the gills will be slow and chemicals will be released from the animal slowly by passive means. Biomagnification of a chemical may take place if no metabolism occurs, with this primarily taking place through the gut of the consumer [(49)]. Muir et al [(50)] reports that biomagnification of hydrophobic compounds such as organochlorine pesticides is more likely to occur in the trophic step from water-breathing prey to air-breathing consumer as the consumer will not have capacity to release the chemical by passive diffusion mechanisms.

While the process of biomagnification is important in the aquatic marine environment, this project primarily focuses on the ability to detect freely available contaminant levels in the water column.

1.4 Sampling of Water for Pollutant Analysis

Water sampling for contaminants analysis can be completed by either direct (Spot sampling) or indirect means (with biomonitor/bioindicator organisms e.g. mussels). Current OSPAR approaches use contaminant data collected from biomonitoring species in order to complete temporal contaminant trend assessments.

The ICES collaborative project as described in this thesis combines passive sampling and biomonitoring techniques. Both approaches can provide valuable information with respect to contaminant levels in the water column and the advantages and disadvantages to both approaches are discussed below.

1.4.1 Traditional Methods

Currently, the most commonly used method for measuring levels of chemical pollutants in water is via the collection of discrete spot/grab/bottle samples, followed by extraction and instrumental analysis. However the ongoing development of techniques such as passive sampling can provide a number of advantages over conventional techniques.

1.4.1.1 Spot Sampling

Generally there are three options available for taking a spot water sample: [11]

1. For surface waters, samples are often collected by directly filling the sample bottle.
2. For deeper water layers, dedicated water samplers are used.
3. Use of e.g., peristaltic pumps for larger volumes of water, with potential for in-line filtration.

Conventional sampling approaches often suffer from several limitations and are not appropriate for long-term monitoring of the presence of organic contaminants in water. The main reasons are as follows: [11, 51 , 52]

1. Provision of a "snapshot" of residues only at the moment of sampling and may fail to detect and account for temporal variation in contaminant concentration. Episodic pollution events can be missed;
2. Chemically-labile or volatile compounds (e.g., chemically-reactive, low-molecular weight compounds, volatile organic compounds, and even some PAHs) can be altered due to microbiological processes, atmospheric air or ultraviolet (UV) radiation during transport and storage of samples; [53, 54]
3. In a grab sample the concentration of a compound is comprised of the truly dissolved compound, the fraction adsorbed to dissolved organic matter and, if the sample is not filtered, a third fraction bound to particles. Thus if simply extracted and analytically determined the concentration is a total of several fractions [55]. The concentrations of the truly dissolved, bioavailable fraction of contaminants are thus not accurately measured by conventional approaches;
4. Aquatic toxicity data and water quality criteria are generally based on dissolved concentrations (which are often not accurately measured);
5. Standard techniques seldom recover enough contaminant mass for bioassays and are often expensive, labour-intensive and time consuming.

1.4.2 New Approaches

Spot sampling is limited in providing a truly representative picture or status of the chemical quality of the water. A more representative picture of water quality can be obtained using new approaches and emerging tools in sampling, including: [56] automatic sequential sampling, continuous on-line/off-line monitoring systems, biomonitor approaches and passive samplers, as discussed herein.

1.4.2.1 Automatic Samplers

Automatic samplers comprise either a set of small bottles which allow collection of a discrete sample every hour or one big bottle which collects sub-samples at different time intervals (composite sample). Main disadvantages include cost and maintenance [11]. Automatic samplers are often impractical since a secure site and significant pre-treatment of water are required. Such systems are rarely used in widespread monitoring programmes [52].

1.4.2.2 Online and Offline Techniques

Such techniques generally involve the use of either an on-line or off line sensing device directly/indirectly immersed in the water body with data collected automatically, and recorded or transmitted telemetrically. Many sensors [57] e.g. multi-parameter probes generally use electrochemical or spectroscopic techniques to acquire continuous data on characteristics of the matrix (e.g., pH, temperature, conductivity, dissolved oxygen, turbidity, and chlorophyll content) [58]. Test kits or immunoassays that can be used with portable instruments are available for various nutrients and a limited range of pollutants, and include colorimetric tests, immunoassays, and a range of sensors.

Most continuous systems are based on optical techniques (i.e. ultraviolet/visible, infrared or fluorescence spectroscopy) using cell or biological test systems. A range of sensors are available, based on electrochemical or electroanalytical technologies. Many are available as miniaturised screen-printed electrodes [59-61]. Due to their cost and vulnerability, the need for a secure site, usually with a power supply, on-line systems are not suitable for widespread deployment in a catchment area [62]. Few devices are capable of trace PAH/PCB measurement.

1.4.2.3 Biomonitor Approaches

Biomonitors can be native organisms collected from a test site or organisms specially deployed at a test site for a known length of time. The measurement of contaminants in their tissues can be used to indicate water quality over a long period. As previously mentioned, the use of mussels as a biomonitor is currently advocated by OSPAR for water quality monitoring purposes.

1.4.2.3.1 Mussels as a Bioindicator Organism – Advantages and Drawbacks

Philips [63], Gosling [64] and Farrington and Trip [65] describe the advantages in using bivalves as bioindicators of contaminant loads in coastal and estuarine systems.

- Bivalves are sedentary and can be long lived [66], and have a wide geographical distribution [66, 67]. Therefore they can be good integrators of chemical contamination in a given area.
- They are relatively tolerant to a wide range of environmental conditions [66] e.g. salinity, season, sampling position in the water column, size, reproductive condition.

- They are relatively tolerant to a wide range of environmental contaminants and can exist in habitats contaminated by a variety of pollutants at the same time. The blue mussel (*Mytilus edulis*) can accumulate PAH in high concentrations without apparent detrimental effects [68].
- Bivalves can bioconcentrate lipophilic contaminants from the aqueous phase by factors of 10^2 to 10^5 [69, 70]. As a result detection limits compared to spot water sampling may be improved [71].
- Provision of a correlation between the degree of pollution and the level of the pollutant in the organisms.
- Fish have microsomal cytochrome P450 enzymes, which enable the biotransformation of PAHs [41]. In contrast, bivalves exhibit low or undetectable activity of enzyme systems that metabolise PAH and PCB, thus allowing the unmetabolised contaminants to be detected in the bivalves' tissues [71]. The contaminant concentrations in the tissues of bivalves thus more accurately reflect the magnitude of environmental contamination. At the same time, bioaccumulation in mussels adequately reflects the changing levels in the environment [63, 72, 73].
- The measurement of chemicals in bivalve tissues provides an assessment of biological availability which is not apparent from measurement of contaminants in environmental compartments (e.g. water, suspended matter, sediment)
- Most bivalves are commercially important therefore a measure of chemical contaminants in their tissues is of public interest.
- Contaminant accumulation by biomonitoring organisms (BMOs) may depend on environmental conditions, such as temperature, salinity, suspended particulate matter, food availability, and levels of oxygen and toxins, as well as on

physiological parameters of the organisms, such as feeding rate, reproductive status, and handling stress [74-78].

- All species accumulate contaminants at different rates under different anatomical, physiological, and behavioural conditions (e.g. sex, lipid mass and composition, feeding habits, respiration rate) [79].
- A period of up to several weeks is necessary for successful salinity adaptation (6-10 weeks were used in the case of this present experiment).
- The combination of water filtration and particle ingestion render bivalves (mussels) liable to POPs present in both the dissolved and particulate phases.

In general the advantages outwiegh the drawbacks and thus it is primarily as a result of these beneficial characteristics that mussels have been selected as bioindicators/biomonitors for use in pollutant monitoring programmes worldwide.

1.4.2.4 Passive Sampling Principles

Passive sampling involves the measurement of analyte concentration as a weighted function of the time of sampling; the concentration of the analyte is integrated over the sampling period [51], as opposed to active sampling which involves the collection of samples at different time intervals using an external energy source (pump). Vrana et al [52] define passive sampling in its broadest sense as any sampling technique based on free flow (according to Fick's first law of diffusion) of analyte molecules from the sampled medium to a receiving phase in a sampling device. The main driving force and separation mechanism are based on the differences in analyte concentration in the two media. The net flow of analyte molecules from one medium to the other continues until equilibrium is established in the system, or until the sampling period is completed [80].

Sampling proceeds without the need for any energy sources other than this chemical potential difference. In passive sampling analytes are absorbed or adsorbed in/on a suitable medium within the passive sampler, known as a reference or receiving phase. This can be a solvent, chemical reagent or a porous adsorbent. The reference/receiving phase is then exposed to the water phase to "sample" the dissolved contaminants [52]. Passive sampling devices can be subsequently extracted in order to derive dissolved phase contaminant concentration information or "extracts" may be of use in biomarker exposure experiments. Within the scope of this project silicone rubber membranes were used as receiving phases, the underlying kinetics and principles of contaminant accumulation and determination are further described in Chapter Two.

1.4.2.4.1 Comparison between the Passive Sampler Approach and the use of Biomonitoring Organisms (BMOs)

Passive samplers have increasingly been used side-by-side with BMOs or as surrogates for BMOs to monitor trace levels of hydrophobic organic chemicals (HOCs) in aquatic environments. Huckins et al [75] provides an overview of such comparative studies.

According to Huckins et al [75], good correlations between analyte concentrations in BMOs and SPMDs exposed side-by-side [81] suggest that passive partitioning and diffusional processes dominate the residue accumulation patterns in the BMOs, whereas poor correlations [82] suggest that active biological processes largely control residue accumulation patterns in the BMOs.

1.5 Objectives/Goals

The objectives/goals of work have been divided into two Sections: (1) The ICES passive sampling trial survey (PSTS) and (2) Ireland's participation in the PSTS. This thesis essentially details the participation of Ireland in the PSTS, with Chapter Three describing the application of silicone rubber PS technologies at two Irish sampling locations, while Chapter Four presents and discusses the Irish results.

1.5.1 Passive Sampling Trial Survey (PSTS)

In 2006, the ICES Working Group on Marine Sediments in Relation to Pollution (WGMS) and the Marine Chemistry Working Group (MCWG) agreed to establish a joint Coordinating Group to organize a collaborative trial for the use of silicone rubber passive samplers (PS) in both water and sediment. Thirteen laboratories participated (twelve from ICES countries and one from Australia).

In order to extend and improve the validation of passive sampling (PS), the passive sampling trial survey (PSTS) programme design included the comparison of data from passive samplers with concentrations of contaminants in organisms exposed to the same environmental compartments. By working at a range of sites within the ICES area, a wide spatial distribution was obtained.

The objectives of the PSTS were to [83]:

- transfer knowledge of PS methodologies within the ICES community,
- gain experience in the use of PS devices,
- estimate the contribution of the analytical component to total variability,

- compare data from PS in water with contaminant concentrations in mussels over a large geographical range in order to validate the environmental relevance of passive sampling data,
- compare PS device uptake rates to those of concurrently deployed mussels.

1.5.2 Ireland's Participation in the PSTS

This thesis is based on the participation of Ireland in the PSTS. The data obtained during this M(Phil) research position, funded by the Dublin Institute of Technology (DIT), the Environmental Protection Agency (EPA) and the Marine Institute (MI), was submitted to the ICES coordinating body and represents Irelands role in the overall ICES project. Ireland, like many other participants, undertook the PS approach in the water phase only.

The basis of this thesis involves a combination of PS and biomonitoring approaches in water to assess the suitability and comparability of their tandem application. The goals of this research project were to:

- complete the analysis of environmentally relevant PCBs and PAHs in both silicone rubber membranes and in biota at test systems deployed in both Dublin and Galway bays;
- determine passive sampling derived water concentrations at the two sites, Dublin and Galway;
- critically assess the application of passive sampling for Irish water quality monitoring purposes;
- develop and validate a GC/MS method for the analysis of the so called 16 USEPA PAHs in *Mytilus edulis* (See Appendix 3).

1.6 References

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CHAPTER 2: USE OF SILICONE RUBBER PASSIVE SAMPLERS TO MONITOR POLYCHLORINATED BIPHENYLS (PCBS) AND POLYAROMATIC HYDROCARBONS (PAHS) IN MARINE WATERS

2.0 Introduction

The majority of aquatic monitoring programmes rely on the collection of discrete grab, spot or bottle samples of water at any given time. Such approaches may be suitable to identify episodic pollution events, but where pollutants are present at trace levels, large sample volumes may be required and subsequent laboratory analysis generally only provides a snapshot of the levels of pollutants at the time of sampling.

Where longer term (temporal) information on contaminant levels is required a number of other approaches may be suitable, e.g. greater frequency of spot sampling (requires filtration and sample pre-treatment for dissolved phase analysis), or analysis of bio-monitor species such as filter feeding mussels which can passively bioaccumulate pollutants from the surrounding water column (knowledge of metabolic effects, sample pretreatment *etc* required). Other approaches include the estimation of pollutant concentrations in water using benthic sediment concentrations followed by modelling using equilibrium distribution co-efficients. A variety of factors can compromise such complicated approaches to derive levels of dissolved analytes (e.g. TOC, bound/unbound contaminants).

Passive sampling methods show greater promise as tools for measuring aqueous (dissolved phase) concentrations of a wide range of priority pollutants and the devices themselves can avoid many of the problems outlined above, since they collect the target analyte *in situ* without altering the bulk solution.

According to Vrana et al [(1)], passive sampling can be defined in its broadest sense as any sampling technique based on the free flow (according to Fick's first law of diffusion) of analyte molecules from the sampled medium to a receiving phase in a sampling device.

In this present study, the medium sampled is the marine water column and the PS receiving phase is silicone rubber (See Section 2.4.3 for further details on silicone rubber).

While passive sampling may often be considered to be more suitable than any of the techniques described above, the principles underpinning and factors governing contaminant uptake and the careful selection of appropriate sampling device must be fully understood and is thus discussed in greater detail below.

2.1 Characteristics of an Effective Passive Sampler

An effective passive sampling device should have the following characteristics [2, 3]: (1) inexpensive to manufacture; (2) small in design and easy to deploy; (3) sensitive to the pollutants which are to be analysed and (4) insensitive to interfering matrix components such as humic material. Further analysis should preferably not involve a high degree of laboratory sample pretreatment or extraction before final analysis. Analyte stability is of great importance e.g. the ability to withstand indefinite storage.

2.2 Advantages and Disadvantages

Passive sampling technology has the potential to become a reliable, robust and cost effective tool [4]. It has a number of advantages and disadvantages, as outlined below.

2.2.1 Advantages of Passive Sampling [1, 3, 4]

- Ability to sample large volumes of water.
- Analyte concentration is integrated over the sampling time, thus allowing for the determination of time-weighted average (TWA) concentrations.
- Passive sampling is less sensitive to accidental, extreme variations of the pollutant concentration.
- Works unattended and independent of a power source
- Can be deployed in a wide range of environments.
- Analytical costs (e.g. pretreatment and frequency) can be reduced substantially.
- Decomposition of the sample during transport, storage *etc* is minimised.
- A single passive sampling device may be suitable for spatial coverage as opposed to multiple spot water samples.
- Passive samplers collect the target analyte in-situ, without affecting the bulk solution.
- Most passive samplers collect only the truly dissolved fraction of chemicals (believed to be the primary concentration available for toxicity, bioaccumulation and degradation [5]) i.e. the bioavailable fraction, since: (a) the truly dissolved molecules become separated from colloids and particles during their diffusion across the membrane that separates water from the receiving phase [6]; and, (b) only dissolved molecules are sorbed by the receiving phase [7].

- Allow for a combination of the control and reproducibility offered by conventional spot water sampling and the time-integration offered by sediment and biota [5].
- More reproducible than live biota, avoiding drawbacks related to migration, mortality, metabolism or selective depuration of contaminants [8]. Also less analytical interference is experienced with PS than with mussel matrix.
- Can be applied to characterise the distribution of organic contaminants between particulate, dissolved and colloidal phases in the water column [9-11].

2.2.2 Disadvantages of Passive Sampling [2]

- Unsuitable for monitoring of short term variations in analyte concentration.
- Lower enrichment efficiency compared to dynamic techniques.
- Sensitivity of enrichment efficiency to temperature fluctuations and water movements, flow rates and biofouling [12].
- The need to determine enrichment factors for individual analytes.
- Impossible to automate (in most cases).
- Validation and quality control can be more complicated than for traditional spot water sampling [4].
- Limitations for compliance testing as the WFD environmental quality standards (EQS) and maximum acceptable concentration (MAC) standards are set for total water (exception: metals), while PS derived water concentrations are given as dissolved water concentrations.

2.3 Principles of Passive Sampling

The process of accumulating a compound in the sampler [5] requires that the chemical compound in the water be carried to the sampler by convection. Mass transfer of analyte then occurs by diffusion from the water to the sampler. Analytes pass through the diffusion limiting membrane pores by conduction. Compounds finally become solubilised in the solvent or sorbed to the selected receiving phase.

2.3.1 Exchange Kinetics

Passive methods may generally be classified as either adsorptive or absorptive [3]. Adsorptive methods take advantage of the physical or chemical retention by surfaces and key parameters involve surface binding and/or surface area. Absorptive methods involve not only surface phenomena but also analyte permeation in the interceding material. This latter approach provides the possibility of compound discrimination due to the membrane's physicochemical characteristics. Pollutant adsorption or absorption from water into most passive sampling systems generally follows the pattern shown in *Fig. 2.1*.

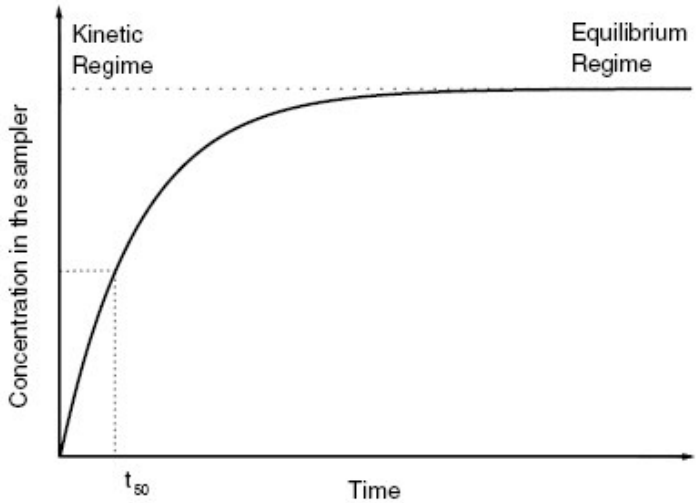

Figure 2.1: Kinetic and equilibrium passive sampling regimes (graphic reproduced from Vrana et al [1]).

The exchange kinetics between a passive sampler and water phase can be described by a first-order, one-compartment mathematical model [1]:

$$Cs(t) = Cw\frac{k_1}{k_2}(1\text{-}e^{-k_2 t}) \qquad \textit{Eqn. 2.1}$$

Where:

$Cs(t)$ is the concentration of the analyte in the sampler at exposure time t,

Cw is the analyte concentration in the aqueous environment, and

k_1 and k_2 are the uptake and offload rate constants, respectively.

Fig. 2.2 presents the two main accumulation regimes, **equilibrium** and **kinetic**, which can be distinguished in the operation of a sampler during field deployment.

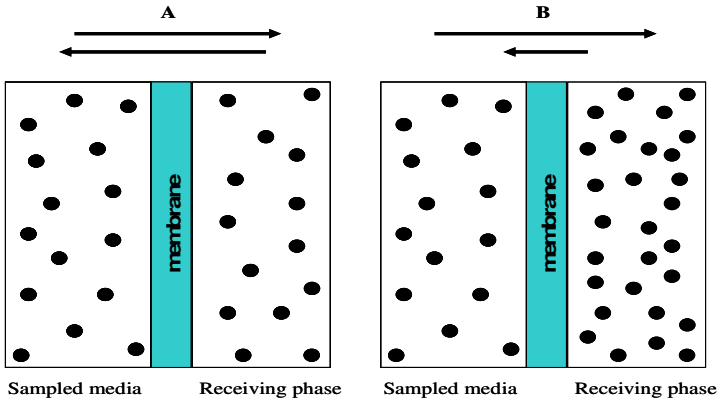

Figure 2.2: Graphical presentation of (a) equilibrium and (b) non-equilibrium (kinetic) passive sampler (graphic reproduced from Kot-Wasik et al [2]).

Based on the concentration gradient of contaminants in the water and on/in the collection phase, contaminants can diffuse into passive sampling devices until equilibrium is reached. Upon achieving equilibrium, further enrichment of contaminants within the sampler can no longer take place. Thus, the time span required until equilibrium is reached depends on the capacity of the collection phase for the contaminants of interest. Passive sampling devices can thus, for practical reasons, be divided into **equilibrium** and **non-equilibrium samplers** [2].

Passive samplers have also been characterised as diffusion-based or permeation-based [13], as they usually work by either diffusion through a well-defined diffusion barrier or permeation through a membrane. Elsewhere, Booij and Smedes [14] characterized hydrophobic passive samplers based on their size, identifying two broad groups; micro and macro samplers. Typical micro samplers are the solid-phase microextraction (SPME) and membrane enclosed sorptive coating (MESCO) while macro samplers include the single phase passive sampling devices which have an organic polymer as their only sequestering phase, e.g. strip samplers made from LDPE (low-density polyethylene), PDMS (polydimethylsiloxane) or POM (polyoxymethylene).

2.3.1.1 Equilibrium Passive Samplers

It is not the purpose of this study to comprehensively review passive sampling, as this has already been completed by others, for example Mayer et al [15] has published a comprehensive overview of equilibrium-passive sampling devices. Equilibrium samplers are characterised by a rapid achievement of equilibrium between contaminants in the water to be sampled and contaminants inside the passive sampler. Thus, in equilibrium sampling [1] the exposure time must be sufficiently long to permit the establishment of thermodynamic equilibrium between the water and the reference phases. In such situations, *Eqn. 2.1* reduces to:

$$Cs = Cw\frac{k_1}{k_2} = CwK \qquad \textbf{Eqn 2.2}$$

Where:

K is the reference phase-water partition co-efficient. Knowledge of *K* allows for the estimation of dissolved analyte concentration.

The basic requirements of the equilibrium-sampling approach are that: [1, 2] stable concentrations are reached after a known response time; the sampler capacity is kept well below that of the sample to avoid depletion during extraction and the device response time needs to be shorter than any pollutant fluctuations in the environmental medium.

Equilibrium sampling devices based on solid-phase microextraction (SPME) [16] have been extensively used to measure dissolved concentrations of pollutants in different matrices [17, 18] and to estimate the bioaccumulation potential in effluents and surface waters [19]. Other frequently used equilibrium samplers include the water-filled polyethylene (PE) bags (PDBS, passive diffusion bag samplers) [20].

2.3.1.2 Non-Equilibrium Passive Samplers

Non-equilibrium samplers are those that do not reach equilibrium with the surrounding water within the sampling period [2]. With kinetic sampling (See *Fig. 2.1*) [1], it is assumed that the rate of mass transfer to the reference/receiving phase is linearly proportional to the difference in the chemical activity of the contaminant between the water phase and the reference phase. In the initial phase of sampler exposure, the rate of desorption of analyte from the receiving phase to water is negligible, the sampler works in the linear uptake regime, and *Eqn. 2.1* reduces to:

$$Cs(t) = Cwk_1t \qquad \textbf{Eqn. 2.3}$$

Eqn. 2.3 can be rearranged to an equivalent relationship:

$$M_S(t) = CwR_St \qquad \textbf{Eqn. 2.4}$$

Where:

$M_S(t)$ is the mass of analyte accumulated in the receiving phase after an exposure time (t) and R_S is the proportionality constant (sampling rate), which is the product of the first-order rate constant for uptake of pollutant (k_1) and the volume of water that gives the same chemical activity as the volume of receiving phase.

R_S may be interpreted as the volume of water cleared of analyte per unit of exposure time by the device. When R_S is known, C_w [the time-weighted average (TWA) concentration of a pollutant in the water phase] can be calculated. For most devices operating in the kinetic mode, R_S does not vary with C_w, but is often affected by water flow or turbulence, temperature and biofouling.

Non-equilibrium samplers are characterized by a high capacity for collecting the contaminants of interest. This high capacity ensures that contaminants can be enriched continuously throughout the sampling period, allowing the TWA over the entire sampling period to be obtained [(2)]. An advantage of kinetic or integrative sampling methods is that they sequester contaminants from episodic events commonly not detected with spot sampling, and can be used where water concentrations are variable. They permit measurement of ultra-trace, yet toxicologically relevant, contaminant concentrations over extended time periods [(1)].

Note: Whether a passive sampler behaves as an equilibrium or non-equilibrium sampler is also dependent on the partitioning properties of the chemicals. Samplers may be in equilibrium for some environmental pollutants during field sampling, while still being in the non-equilibrium phase for other compounds [(21)].

2.4 Available Water Passive Samplers

Several novel passive sampling devices suitable for monitoring a range of non-polar and polar organic chemicals, including pesticides, pharmaceutical/veterinary drugs and other emerging pollutants of concern have been developed. Marine applications for monitoring hydrophobic organic pollutants by semi-permeable membrane devices (SPMDs) [6], the Chemcatcher [22], Ceramic Dosimeters [23], the Membrane Enclosed Sorptive Coating (MESCO) [24] and the Polar Organic Chemical Integrative Sampler (POCIS) [25] have all been documented.

As the SPMD and POCIS have found greater application and received greatest attention in the literature, they are described in more detail below. While less information is available for the application of silicone rubber membranes for the monitoring of hydrophobic contaminants, based on available research it was shown that silicone rubber PS shows good potential for the pollutants of interest in this project and is thus the passive sampler of choice in this current ICES study.

2.4.1 Semi-Permeable Membrane Devices (SPMDs)

The design of the SPMD was first published in 1990 [26] and they operate on the principle of a high surface-to-volume ratios and sample between 0.5 and 15 L of water per day [27] enabling detection of ambient sub ng/l concentrations of highly hydrophobic compounds [5]. SPMDs generally comprise a low-density polyethylene (LDPE) tube filled with approximately 1ml of high molecular weight lipid, typically high purity synthetic triolein (1,2,3-tris-cis-9-octadecenoyl glycerol) which has a high capacity for compounds with Log octanol-water partition co-efficients (Log K_{ow}) >3 [6]. *Table 3.7* indicates that the PCBs and PAHs of interest in this current study would be suitable for sampling by SPMDs, as they all have a Log K_{ow} value of >3. Operation is based on the

diffusion of compounds though the polymeric membrane bag and their accumulation in the lipophilic solvent. Solute size limitation excludes large molecules as well as those that are adsorbed on colloids or humic acids.

Only truly dissolved and non-ionized contaminants diffuse through the LDPE membrane and can be separated by the sampler i.e. only the bioavailable fraction of pollutants in waters are absorbed and not compounds bonded to macromolecules. SPMDs are often used as an indicator of the bioavailability of hydrophobic contaminants in the environment [(3)]. SPMDs have successfully been tested for non-polar and moderately polar organic pollutants in water, including PAHs, PCBs, PCDDs, PCDFs and several OCPs [(8)].

Devices made from silicone tubing or low density polyethylene (LDPE) tubing without solvent or resin have been applied by Booij et al [(28)] as alternatives to SPMDs. Some simplicity in preparation and post-deployment procedures and in interpretation is offered by the omission of the lipid receiving phase of the SPMD. Several authors [(28-31)] have shown that LDPE membranes (i.e. triolein-free SPMDs) are just as efficient in sampling organic compounds with Log $K_{ow} > 6$ as are SPMDs, both in the laboratory and in the field. For compounds with a Log $K_{ow} < 6$ the amounts absorbed by LDPE membranes are smaller than for SPMDs because of the smaller sorption capacity of LDPE membranes [(32)]. LDPE strips and SPMD devices have been tested for accumulation studies on petroleum biomarker compounds, as they can discriminate between petroleum sources [(33)].

While the LDPE film of the SPMD is highly resistant to biodegradation, its strong hydrophobicity depresses the sampling rate of target compounds in the water phase. Conversely, cellulose membranes can achieve equilibrium more quickly than polymeric

films, such as LDPE, because cellulose polymers possess hydrophilic groups i.e. hydroxyls [34- 36].

The SPMD is probably the most widely used PS device in circulation, having been used to test a wide variety of compounds in a range of different environments.

The SPMD was not used in the PSTS simply because this survey was a trial to provide an opportunity to validate a relatively new sampler for PCB and PAH contaminants in seawater. This has already been completed for SPMDs. Benefits of using the silicone rubber strips ((PDMS) See Section 2.4.3) over using the SPMD include: less expense (as triolein not required), simplification of extraction procedure (as only membrane extracted as opposed to membrane and triolein), manufacturing is less complicated and PDMS are easier to clean for re-use.

Although LDPE film has similar advantages over the SPMD, it was not used in this trial as it is more widely used than PDMS. This trial can be viewed as an attempt to validate and in turn promote the use of a new upcoming PS device, the PDMS.

2.4.2 The Polar Organic Chemical Integrative Sampler (POCIS)

The POCIS [37] was designed to mimic respiratory exposure of aquatic organisms to dissolved chemicals without the inherent problems of metabolism, depuration of chemicals and mortalities of test organisms at highly contaminated sites. POCIS, like other passive sampling devices, thus provides a worst-case exposure scenario for aquatic organisms, enables concentration of sufficient amounts of bioavailable hydrophilic organic chemicals for some biomarker tests, and permits determination of the biologically relevant TWA concentrations in water [38]. It can be used to monitor

hydrophilic contaminants, such as pesticides, prescription and over-the-counter drugs, steroids, hormones, antibiotics and personal-care products [25] and permits determination of TWA concentration in water over extended periods (several weeks).

As POCIS is generally used for sampling of the more water soluble compounds (Log K_{ow} <3), it was an unsuitable device for use in this current study where the compounds of interest (PCBs and PAHs) have Log K_{ow} values of >3 (See *Table 3.7*).

2.4.3 Silicone Rubber Passive Samplers

According to Smedes [39], any material with a non-polar structure can essentially function as a passive sampler (PS). Rusina et al [40] discussed the properties of materials for passive samplers and proposed that silicone rubbers can be attractive reference phases due to their high partition co-efficients and low transport resistances. Silicone rubber passive samplers consist of polydimethylsiloxane (PDMS) sheets, secured to a stainless steel frame. Section 3.3 provides details on the assembly of this passive sampling device, as was utilised in this current study. The chemical structure of PDMS is shown in *Fig. 2.3* below.

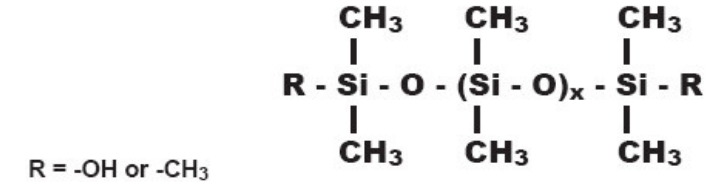

Figure 2.3: Chemical structure of the Polydimethylsiloxane (PDMS) polymer (Graphic reproduced from Ushakova and Van Roy [41]).

According to Yates et al [42], by using a silicone rubber reference phase that equilibrates with the surrounding medium, the partition co-efficient can be used together with the concentration in the sampler to: (1) determine the freely dissolved concentration in the environmental medium [15]; (2) to estimate the sampling rates of added performance

reference compounds (PRC) [43] that have dissipated from the passive sampling device and subsequently the equilibration rate constants which are used to determine the sampling scenario (kinetic or equilibrium), as not all compounds would have attained equilibrium.

Yates et al [42] measured the Log silicone rubber-water partition co-efficients (Log $K_{sr,w}$) of a series of hydrophobic organic compounds (PCBs and PAHs), with Log octanol-water partition co-efficients (Log K_{ow}) values for the compounds studied ranging from 3.3 to 8.2 (See *Table 3.7*). The co-solvent method [44, 45] was used, with methanol as co-solvent. Yates et al [42] describes this method in detail. Strong linear relationships were found with literature values for the corresponding Log K_{ow} for both PCBs and PAHs (See *Table 3.7*). This confirmed that partitioning into the silicone rubber is strongly determined by compound hydrophobicity. This in turn suggests that Log K_{ow} is a good predictor of Log $K_{sr,w}$ and that absorption is the main mechanism for accumulation of analytes into the silicone rubber polymer [42].

The application of silicone rubber passive samplers for monitoring hydrophobic contaminants has been gaining importance in recent years. Key contracting parties to OSPAR have developed and utilised this technique [39] and wished to further investigate whether the technique would be easily transferred between other laboratories. As a result, the ICES working groups on Marine Sediments (WGMS) and Marine Chemistry (MCWG) established a joint co-ordinating group which organised a passive sampling trail survey (PSTS) using silicone rubber passive samplers in water and sediment (See Section 3.0 for further details on the PSTS).

This thesis discusses the application of silicone rubber passive sampling devices in water and further utilises the PRC concept and the linear relationship between Log K_{ow} and Log $K_{sr,w}$ to determine dissolved water concentrations of PCBs and PAH at two Irish marine sites.

2.5 Factors Influencing Passive Sampler Performance

For a good sampler performance, a sufficiently high sampling rate, i.e. the rate at which the sampler accumulates chemicals from water is essential. High sampling rates are needed especially for non-polar chemicals due to their low concentration in the water column (<1ppb) [46]. The uptake rates of contaminants into PS devices in general are affected by several factors including the sampler design (type and properties of the membrane), the physicochemical properties of the analyte (Section 2.7) and environmental conditions prevailing during sampling [46, 47].

2.5.1 Sampler Design

Bi-phase and single-phase passive sampling devices have been developed. The two phase PS, e.g. SPMD, typically consist of a receiving phase, with a high affinity for organic contaminants, separated from the aqueous environment by a diffusion limiting membrane. In the case of the single phase PS, e.g. silicone rubber (PDMS), the sheet of polymeric material acts as both the receiving phase and the diffusion limiting membrane. The assembly of the PMDS passive sampling device used in this study is detailed in Section 3.3.

The rate-limiting step in the uptake to the receiving phase (in the absence of fouling) may be controlled by diffusion in the diffusion-limiting membrane or across the aqueous diffusive boundary layer at the membrane-water interface [48]. When applying passive samplers in the aqueous environment, the thickness of the water boundary layer can vary from 1 mm to <1 µm for quiescent and highly turbulent conditions, respectively [43].

2.5.2 Environmental Factors

Water sampling rates (R_S) of specific analytes by passive samplers depend on a complex set of interacting environmental variables, including (inter alia) temperature [46, 49-51], site hydrodynamics (water flow/velocity/turbulence) [24, 29, 43, 47], biofouling impedance [43, 52, 53], sorption of the compounds to dissolved organic carbon (DOC), photo-degradation, and the geometry of the mounting cages [43]. The potential effects of such environmental variables must be better defined in order to more accurately estimate ambient chemical concentration data. The site specific environmental conditions affecting the PS devices deployed as part of this current study are included in *Table 4.3*.

2.5.2.1 Temperature/Water Flow

Variations in temperature and water flow rates can reportedly cause up to 4 to 10-fold differences in membrane/device sampling rate, due to variations in analyte uptake rates and facial velocity - turbulence effects, especially for compounds with Log K_{ow} values >4.4 [50, 54], because uptake is heavily influenced by the external water boundary layer (WBL) [27].

2.5.2.1.1 Temperature

Petty et al [55] found that there were only small differences in PAH uptake rate by SPMDs at temperatures tested (10, 18, and 26) °C. Huckins et al [49] found that while temperature effects (10, 18, and 26) ^{o}C on sampling rate (R_S) values for 15 priority PAHs by SPMDs appeared to be complex, they were also relatively small. Uptake rates by SPMDs were found to increase by a factor of ~2 for each 10 °C temperature increase [49-51]. On average, Booij et al [50] reported higher sampling rates (R_S) at 30 °C than at 2

°C by a factor of 2.8, which is of the same order as the 1.5-fold increase in PAH sampling rates between (10 and 26) °C reported by Huckins et al [49]. SPMD-water partition co-efficients did not significantly change with temperature, but LDPE-water partition co-efficients were larger at 2 °C than at 30 °C by a factor of 2 [50].

During work carried out by Smedes [39] on silicone rubber, he found that the 30 % decrease in sampling rate (R_S) for 10 ^oC decrease in temperature experienced was in agreement with the observations by Booij et al [56], who found a 100 % increase in sampling rate (R_S) with a 30 ^oC increase in temperature.

2.5.2.1.2 Hydrodynamics

Water turbulence affects the thickness of the unstirred layer of water that forms part of the diffusion-limiting barrier near the sampler surface [1]. Since mass-transfer resistance is directly proportional to boundary layer thickness, the sampling rates of analytes will vary with the hydrodynamics of the deployment site [54].

2.5.2.2. Biofouling

Any unprotected surface submersed in an aqueous ecosystem will eventually become a substrata for bacteria, flora and fauna, which may ultimately form a biofilm [1, 5]. The composition and thickness of this biofilm will depend on the aquatic system and they can be very variable. It is important to note that there are marked temporal variations in fouling [57]; the growth of fouling species may be suppressed in the winter and then increase rapidly during the summer when the temperature is higher.

Aquatic biofouling is considered to comprise four stages; (1) the adsorption of a conditioning layer, (2) adhesion of bacteria, (3) growth of a biofilm and (4) macrofouling [58]. Within minutes of immersion of a substrate in water, the substrate will be coated with a layer of organic molecules such as sugars and proteins. The next stage of biofouling involves colonisation of the surface by bacteria, which occurs in a matter of hours. The bacteria then secrete a variety of sticky substances called extracellular polymeric substances (EPS), thus, the substrate is coated with a biofilm. This biofilm traps other species such as algal spores and marine fungi. Finally, larger marine invertebrates e.g. barnacles, mussels, seaweed will attach and grow on the membrane surface; this is termed macrofouling and can occur over days and/or weeks [59].

Biofouling affects the overall resistance to mass transfer by increasing the thickness of the barrier and blocking any water-filled pores in the diffusion-limiting membranes [1]. Colonising organisms may damage the surface of the membrane if it is made of degradable material and may impede the uptake of contaminants [54, 60].

Booij et al [53] found that extreme biofouling (1) does not always result in reduced sampling rates, (2) does not preclude the existence of flow effects on the sampling rates, and (3) differences in uptake rates are quantitatively reflected by the dissipation rates of Performance Reference Compounds (PRCs) as discussed further below.

2.6 Introduction to Performance Reference Compounds (PRCs)

Huckins et al [54] and Booij et al [29] have shown that the effect of environmental factors (biofouling, temperature, and flow velocity-turbulence) on the uptake kinetics can be accounted for by measuring the dissipation rate of performance reference compounds (PRCs).

PRCs are generally labelled or unlabelled, analytically non-interfering organic compounds, that have moderate to relatively high fugacity, and are added to the sampler prior to deployment [27]. Compounds commonly used as PRCs include perdeuterated priority pollutant PAHs, with no larger molecular weight than chrysene-d_{12} (M_W: 240.36), 2,2'-dichlorobiphenyl (M_W: 222) and 2,4,5-trichlorobiphenyl (M_W: 256)[54]. Two PRCs used in this study (i.e. benz[e]pyrene-d_{12}, perylene-d_{12}) had molecular weights greater than those mentioned above, both of which were found not to be suitable for the purpose of sampling rate (R_S) determination as no dissipation occurred during the course of the study period (Dublin). It is assumed that this is related to the lower sampling rate determined at Dublin (2.38 litres per day (l/d)) compared to Galway (8.48 l/d).

The remaining deuterated PAHs used as PRCs in this project include: naphthalene-d_8, fluorene-d_{10}, phenanthrene-d_{10}, fluoranthene-d_{10}, chrysene-d_{10} and coronene-d_{12}. Certain PCBs such as PCB 10, 14, 21, 30, 50, 55, 78, 104, 145 and 204 (as utilised in this project) have also been used as PRCs. The levels of such PCBs are either negligible or not commonly found in biota or environmental samples and are thus suitable for selection as PRCs for environmental monitoring. When environmental conditions at an exposure site differ from laboratory calibration conditions or calibration data are not

available, samplers spiked with PRCs serve as a type of QC sample, providing information about in situ uptake kinetics [29, 54].

This novel *in situ* calibration approach is based on theory and experimental evidence that *in situ* PRC dissipation rate constants at sampling sites are related to the uptake rate constants of target compounds [54], i.e. the rate of PRC losses is proportional to the rate of analyte uptake.

The *in situ* sampling rate (R_S) is the critical factor for contaminant sampling by passive samplers and information on this parameter can be obtained from the dissipation of the PRCs [29, 43, 54, 60]. Estimation of water sampling rates from the PRCs' dissipation parameters provides a means to evaluate the influence of the exposure variables on the uptake kinetics of the analytes. Mechanisms to complete R_S calculations are further described throughout this thesis.

Booij et al [32] report that the PRCs also allow for the identification of compounds that attain sorption equilibrium during the exposure. For example, a PRC with a Log K_{ow} of 5 that is completely dissipated indicates that all analytes with similar and lower hydrophobicity have attained sorption equilibrium, and aqueous concentrations of these compounds should be calculated using an SPMD-water partition co-efficient. On the other hand, when a PRC with a Log K_{ow} of 6 is completely retained, then all analytes with similar and higher Log K_{ow} are in the linear uptake phase, and aqueous concentrations should be calculated using the apparent water sampling rates of the SPMD.

2.7 Pollutants of Interest

The primary target analytes of interest are polychlorinated biphenyls (PCBs) and polyaromatic hydrocarbons (PAHs), both of which are discussed below.

2.7.1 Polychlorinated Biphenyls (PCBs)

2.7.1.1 Structure

PCBs are a class of 209 manmade, organic chemical compounds in which chlorine (Cl) atoms are attached to a biphenyl molecule ($C_{12}H_{10}$). Biphenyl is a dual-ring structure comprising of two 6-carbon benzene rings linked by a single carbon-carbon bond. The chemical formula for PCBs can be represented as $C_{12}H_{10-n}Cl_n$, where n is the number of chlorine atoms within the range of 1 (mono) to 10 (deca). Breivik et al [61, 62] report that greater than 70% of the global production of PCBs is represented by tri-, tetra-and pentachlorinated biphenyls.

2.7.1.2 Uses/Sources of PCBs

Polychlorinated biphenyls were commercially produced as complex mixtures for a variety of applications, including dielectric fluid for capacitors and transformers, heat transfer fluids, hydraulic fluids, lubricating and cutting oils and as additives in pesticides, paints, adhesives, sealants and plastics. The main sources of PCBs to the marine environment include energy production, combustion industries, production processes and waste (landfill, incineration, waste treatment and disposal). Many countries and intergovernmental organizations have now banned or severely restricted the production, use, handling, transport and disposal of PCBs.

2.7.1.3 Nomenclature

The positions of the chlorine substituents on the rings are denoted by numbers assigned to each of the carbon atoms, with the carbons supporting the bond between the rings being designated 1 and 1' (See *Fig. 2.4*).

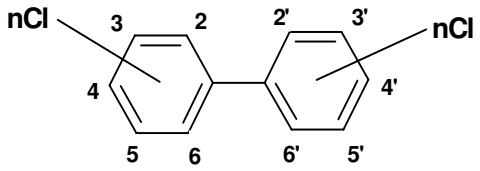

Figure 2.4: The structure of PCB congeners.

The position of the chlorine expressed in terms of its relationship to the carbon-to-carbon bond between the two aromatic rings defines whether PCBs are stated to be in the ortho, meta and para position (See *Fig. 2.5*).

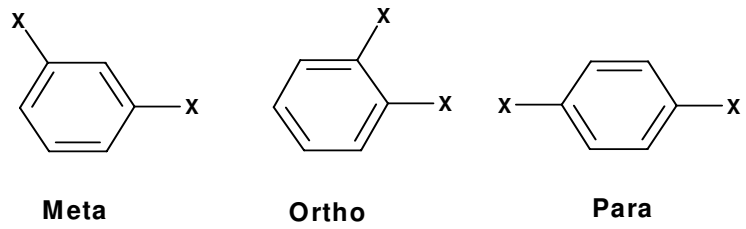

Figure 2.5: Meta, ortho and para positions on benzene ring.

Rotation of the benzene rings around the bond connecting them further define PCBs ultimate configurations as either planar: where the two benzene rings lie in the same plane or non-planar: where the benzene rings lie at 90° angle to each other.

Two different systems exist for naming PCBs: the International Union of Pure and Applied Chemistry (IUPAC) system and the Ballschmiter and Zell [63] system. The use of full chemical names as proposed by the IUPAC system can be unwieldy (e.g. 2, 3, 3', 4, 4', 5 - pentachlorobiphenyl), while Ballschmiter and Zell [63] arranged the 209 PCB

congeners in ascending numeric order and assigned each a "Ballschmiter" number from 1 to 209 (e.g. PCB 156). This latter naming system is internationally utilised in monitoring programmes and throughout this thesis.

2.7.1.4 Properties

Most pure PCB congeners are colourless, odourless crystals and can range in chlorine content from 19 to 70% [64]. PCBs generally have low water solubilities, low vapour pressures, and are soluble in most organic solvents, oils and fats. The major characteristic controlling the bioaccumulation of PCBs in the tissues of aquatic organisms is the compound's hydrophobicity, as represented by the octanol-water partition co-efficient (K_{ow}) (See *Table 3.7* for Log K_{ow} values). Congeners with a lower degree of chlorination are more soluble and volatile than those with high percentage chlorination [64].

The chemical and physical stability of PCBs have been responsible for their continuing low-level persistence in the environment. The individual PCBs differ in persistence in the environment and in their toxicological mechanism and potency depending on the chlorine number and the substitution pattern of the biphenyl rings [65]. Some PCBs (co-plane) have been identified as "dioxin-like" with relative toxicities 100-1000 times higher than those associated with others PCB congeners. These PCBs just like dioxins/furans have been allocated toxic equivalency factors (TEFs) [64] relative to the most potent dioxin 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD).

2.7.1.5 Human Exposure

It is currently assumed that the general population receives its major exposure to PCBs through food intake. Since PCBs are lipophilic and accumulate in the food chain, foods of animal origin are an important source of exposure. Intake of fatty fish from contaminated waters may significantly increase the daily intake of PCBs e.g. Swedish fishermen active in the Baltic Sea and with much higher than average intakes of herring and salmon were found to have blood levels of PCBs two times higher than those in the general population [(66)].

The European Food Safety Authority (EFSA) has concluded that no health based guidance value for humans can be established for non dioxin-like PCB because simultaneous exposure to non dioxin-like and dioxin-like compounds hampers the interpretation of results from toxicological and epidemiological studies, and the database on effects of individual non dioxin-like PCB congeners is rather limited [(67)].

2.7.2 Polyaromatic Hydrocarbons (PAHs)

2.7.2.1 Structure

PAHs are composed of 2+ aromatic rings which are fused together when a pair of carbon atoms is shared between them [(68)]. The resulting structure is a molecule where all carbon and hydrogen atoms lie in one plane. Naphthalene ($C_{10}H_8$), consisting of two fused aromatic rings, is the lowest molecular weight PAH. It is worth noting that according to the International Union of Pure and Applied Chemistry (IUPAC), PAHs are composed of 3+ aromatic rings and thus naphthalene is not recognised as a PAH compound.

2.7.2.2 Uses/Sources of PAHs

PAHs primarily come from two main sources: (a) petrogenic, including fossil fuels, mainly crude oils, bituminous deposits, petroleum products; and (b) pyrogenic, products of incomplete combustion formed during natural combustion processes, mainly forest fires, from combustion of fossil fuels, coal and peat, from the incineration of agricultural, industrial and municipal waste [69], from Power stations and motor vehicles [70]. It should be noted that a number of biogenic PAHs exist, for example perylene, which are outside the scope of this project.

Petrogenic PAHs are characterized by families of related PAH homologues (naphthalenes, fluorenes, phenanthrenes, dibenzothiophenes, and chrysenes) in which the unalkylated or parent PAH for each family is less abundant than the alkylated homologues [71]. A high proportion of lighter, alkylated 2- and 3- ring PAHs [69, 72, 73] and a lower proportion of 5- and 6- ring PAHs [74] is indicative of a petrogenic source (e.g. unweathered oil). This is further discussed in Section 2.7.2.2.1.

Parent PAHs are mainly produced by pyrolysis [72]. In general, pyrolytic PAHs are the dominant source of PAHs in the marine environment [74]. Pyrolytic sources are primarily dominated by the heavier, more persistent 4-6 ring compounds [69, 72, 73], with a high proportion (>40%) of parent (unalkylated) PAH [73]. Fluoranthene and pyrene are two of the most abundant pyrogenic compounds [75].

In general, petrogenic PAHs are considered to arise from point sources and to be distributed on a local scale. In contrast, pyrogenic PAHs are more diffuse and are distributed on a wider scale.

2.7.2.2.1 Sources Identification – PAH Concentration Ratios

PAHs have different distribution patterns according to their production sources [73]. It is possible to distinguish between petrogenic (fossil fuels) and pyrogenic (incomplete combustion of organic materials) PAHs by studying a variety of PAH concentration ratios. A number of different indices have been developed to assess the different origins of these compounds, [76- 81] a summary of which are presented in *Table 2.1*.

Table 2.1: Typical PAH concentration ratios for pyrogenic and petrogenic origins (Table reproduced from Webster et al [69])

Origin	P/A	Fl/Py	MP/P	(Fl+Py)/(MFl+Mpy)
Pyrogenic	<10	>1	<1	~3
Petrogenic	>10	<1	>1	<3

P/A: phenanthrene/anthracene; Fl/Py: fluroanthene/pyrene; MP/P: methylphenanthrenes/phenanthrene; (Fl+Py)/(MFl+MPy): (fluoranthene+pyrene)/(methylfluoranthene+methylpyrene).

Isomer ratios such as phenanthrene/anthracene (P/A) and the fluoranthene/pyrene (Fl/Py) ratio can help identify pyrogenic sources [69]. Phenanthrene and pyrene are more thermodynamically stable than anthracene and fluoranthene, resulting in a higher proportion of these compounds if the source is petrogenic [82]. The phenanthrene/anthracene (P/A) ratio is the most often used [76-78]. The P/A ratio is temperature dependent and decreases with increasing temperature, thus high temperature processes can be characterized by low P/A values (<10). The slow thermal maturation of organic matter in petroleum is governed by thermodynamic properties and leads to much higher P/A values (>10). The P/A ratio for crude oils is normally close to 50 [69]. It must be noted however that high P/A ratios can also be found in sediments from remote areas as a result of selective photo-oxidation of anthracene during its long range atmospheric transportation and therefore the P/A ratio is less reliable as a source input indicator [83-85]. Similarly, the fluoranthene/pyrene (Fl/Py) ratio is often used to distinguish between pyrogenic and petrogenic sources [77, 78] with values of >1 being associated with pyrogenic origins [69].

The comparison of alkylated PAHs with the parent compound, using the methylphenanthrene/phenanthracene (MP/P) and (fluoranthene + pyrene)/ (methylfluoranthene + methylpyrene) (Fl+Py)/(MFl+MPy) indices can be used to help identify petrogenic contamination [69] (See *Table 2.1*). Alkylated homologues are deficient in combustion generated PAHs, giving an MP/P ratio of <1. (Fl+Py)/(MFl+MPy) values of near 3 have been found in sediments where the main source of contamination is pyrolysis, with lower values indicating a smaller pyrogenic and greater petrogenic input [81]. However alkylated PAHs were outside the scope of this project.

2.7.2.2.2 PAH Ratio Plots

Baumard et al [77, 86] demonstrated that by plotting the Fl/Py ratio against either the MP/P ratio or the P/A ratio a petrogenic and a pyrogenic zone could be identified (See *Fig. 2.6*). The zones defined by high Fl/Py ratios (>1) and low P/A (<10) or MP/P (<2) ratios are characteristic of pyrogenic PAHs (top left quadrant). In contrast, a low Fl/Py ratio and high P/A or MP/P ratio is characteristic of petrogenic PAHs (bottom right quadrant) [87]. The other two quadrants may indicate a mixed source of PAHs.

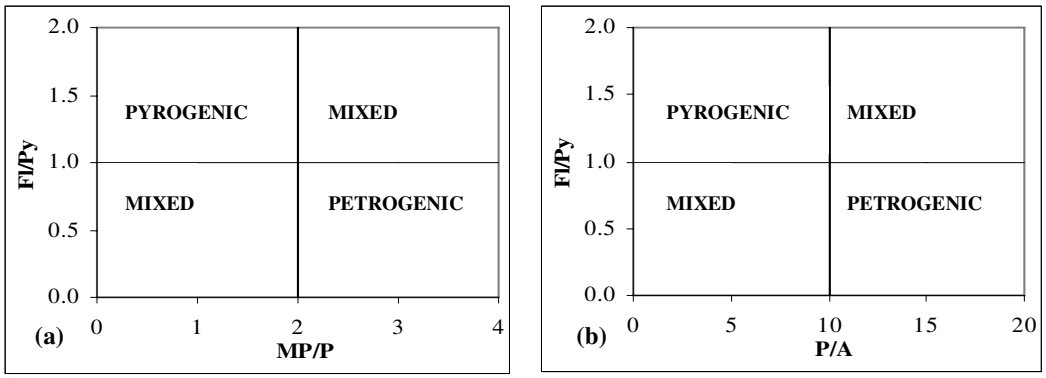

Figure 2.6: Source identification plots of (a) fluoranthene/pyrene ratio (Fl/Py) against the methylphenanthrene/phenanthrene ratio (MP/P) and (b) the fluoranthene/pyrene ratio (Fl/Py) against the phenanthrene/anthracene ratio (P/A).

Several PAHs exist as alkyl homologues, with the parent nonalkylated compound (C0) and monoalkylated (C1), dialkylated (C2), trialkylated (C3), and tetraalkylated (C4) compounds. The relative abundance of these homologues being indicative of the source of the PAH and the degree of weathering [88-93]. Highly weathered oils often exhibit the profile C0 <C1 < C2 < C3 < C4 [33].

As chrysene and benzo[a]pyrene are photo-labile, light must be excluded from extracts and standard solutions containing these compounds; and as pyrene fluorescence may be quenched by oxygen great care must be taken to deoxygenate solvents in analyses using HPLC with fluorescence detection [94].

2.7.2.3 Nomenclature

Several systems of nomenclature have been used to describe PAH ring structures with the International Union of Pure and Applied Chemistry (IUPAC) being the most widely accepted format. The most important rules of the IUPAC system are described briefly below. For further details on the IUPAC rules, visit the following website: http://www.acdlabs.com/iupac/nomenclature/79/r79_2.htm [95].

1. PAH structures are typically orientated such that the greatest possible number of rings in a row are aligned horizontally, with the maximal number of rings positioned in the upper right quadrant and the minimal number of rings positioned in the lower left quadrant (See *Fig. 2.7A*).
2. Carbon atoms are numbered in a clockwise direction starting with the carbon atom that is not part of another ring and is in the most counter-clockwise position of the uppermost ring farthest to the right. Carbon atoms common to two or more rings are not numbered (See *Fig. 2.7B*).

3. Atoms which are common to two or more rings are lettered in alphabetical order with the side between carbon atoms 1 and 2 designated "a". Alphabetical order is continued clockwise around the molecule. Interior atoms follow the highest number, taking clockwise sequence wherever there is a choice.
4. Compounds (or Isomers) formed by the addition of a component are distinguished by letters and numbers enclosed in square brackets, which are placed immediately after the name of the added component. This is in order to describe where the constituent group is attached or where a ring is fused to the face of the molecule. Appropriate letters are used where a ring is fused to more than one face of the molecule.

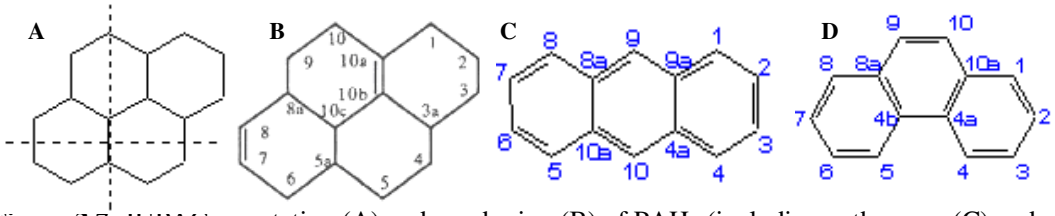

Figure 2.7: IUPAC orientation (A) and numbering (B) of PAHs (including anthracene (C) and phenanthrene (D) which depart from these rules of nomenclature).

2.7.2.4 Properties

The physical and chemical characteristics of PAHs vary with molecular weight (See *Table 2.2*). For instance, PAH resistance to oxidation, reduction and vapourisation increases with increasing molecular weight, whereas the aqueous solubility of these compounds decreases [96]. As a result, PAHs differ in their behaviour, distribution in the environment, and their effects on biological systems (See Appendix 3 for further details on distribution of PAH in the environment).

PAHs can be divided into two groups based on their physical, chemical and biological characteristics. The lower molecular weight PAHs (2- to 4-rings) generally exhibit little or no carcinogenic potential [97], but are of concern due to their acute toxicity or tainting

properties [70, 98, 99]. However, some higher molecular weight PAHs (4- and 6-rings) are known to be both highly mutagenic and carcinogenic (See Section 2.7.2.5).

Table 2.2: Physical-chemical characteristics of the 16 US EPA PAHs

PAH (Symbol)	Molecular Weight	No of rings	Water solubility (g/m^3)	Log K_{ow}	Vapour Pressure at 20 °C (mm Hg)
Naphthalene (N)	128.2	2A	30.2	3.35	1mm Hg at 53 °C
Acenaphthylene (Acy)	152.2	2A1C	3.93	3.61	$9.12*10^{-4}$mm Hg at 25°C
Acenaphthene (Ace)	154.2	2A1C	3.93	3.92	0.0027
Fluorene (F)	166.2	2A1C	1.9	4.18	0.013
Phenanthrene (P)	178.2	3A	1.18	4.52	$6.8*10^{-4}$
Anthracene (A)	178.2	3A	0.076	4.50	$1.96*10^{-4}$
Fluoranthene (Fl)	202.3	3A1C	0.26	5.20	$6*10^{-6}$
Pyrene (Py)	202.3	4A	0.135	5.00	$6.85*10^{-7}$
Benzo[a]anthracene (BaA)	228.3	4A	0.011	5.91	$5*10^{-9}$
Chrysene (C)	228.3	4A	0.0019	5.86	$6.3*10^{-7}$
Benzo[b]fluoranthene (BbF)	252.3	4A1C	0.014	5.78	$5*10^{-7}$
Benzo[k]fluoranthene (BkF)	252.3	4A1C	0.008	6.11	$5*10^{-7}$
Benzo[a]pyrene (BaP)	252.3	5A	0.0038	6.35	$5*10^{-7}$
Indeno[1,2,3,-cd]pyrene (IP)	276.0	5A1C	0.0005	7.66	$1*10^{-10}$
Benzo[ghi]perylene (BghiP)	276.3	5A1C	0.0003	6.90	$1*10^{-10}$
Dibenzo[ah]anthracene (DahA)	278.4	5A	0.0005	6.75	$1*10^{-10}$

Molecular weight, ring (A=aromatic, C= nonaromatic) and water solubility data taken from Huckins et al [49]. Log Kow data taken from Sangster [100] and vapour pressure data taken from Verschueren [101, 102].

2.7.2.5 Human Exposure

Human exposure to PAH arise generally from atmospheric and aquatic pathways, including the human health risk posed via the consumption of contaminated food products. The carcinogenic effects of PAHs are reputed to vary with the physiochemical properties of the individual PAH analyte. Some 4- and 6-ring PAHs are known to be both highly mutagenic and carcinogenic, e.g. benz[a]anthracene, benzo[a]pyrene and dibenz[a,h]anthracene [70, 72, 103-106] and some of their metabolites may potentially produce potent xenobiotic activity [97]. Xenobiotic activity may often be centred in the intestinal epithelia, bone marrow, lymphoid organs and testes [107].

As regards the carcinogenic effects of PAHs, Luch [108] compiled information from articles written by some of the most recognizable PAH researchers. Topics covered in this book include: exposure to and biomonitoring of PAHs in the human population; metabolic activation of PAHs; genotoxicity and repair of PAH-induced DNA damage; and factors modulating individual susceptibility to the deleterious effects of PAHs.

2.8 ICES Passive Sampling Trial Survey (PSTS)

In 2006, the ICES working groups on Marine Sediments (WGMS) and Marine Chemistry (MCWG) agreed to establish a joint coordinating group to organise a collaborative trial of the use of silicone rubber passive samplers in water and sediment. The overall project was titled the passive sampling trial survey (PSTS), having a total of 13 participating laboratories (12 from ICES countries and one from Australia). (See Section 3.0 for further details or Annex 7 of the ICES MCWG Report 2007 [(109)])

This thesis in fulfilment of the ICES passive sampling initiative primarily describes the application of biomonitoring (transplantation of blue mussels) in addition to the concurrent deployment of silicone rubber passive sampling membranes at two Irish coastal test sites (Galway Bay and Dublin Bay). As Ireland participated solely in the water phase PS section of the trial, details on the sediment sampling will not be discussed herein (SeeSection 1.5.2 for thesis goals).

2.9 References

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CHAPTER 3: MATERIALS AND METHODOLOGIES EMPLOYED TO FULFIL IRELAND'S ROLE IN THE ICES PASSIVE SAMPLING TRIAL SURVEY (PSTS)

3.0 Passive Sampling Trial Methodology and Concepts

The described passive sampling trial survey (PSTS) was conducted as part of an ICES (eleven countries and thirteen laboratories) inter-calibration exercise to investigate the merits of such approaches. All participants of the study used the same standardised procedures (as per guidance document located on the PSTS website [(1)]) for the assembly, deployment, retrieval and disassembly of the passive samplers.

In this survey, the passive sampling of the water phase was completed in parallel with deployment of mussels, to investigate the relationship between contaminant uptake in mussels and passive sampling results on a wide geographic scale. The objective was to compare the results of the passive sampling of the water mass with the results obtained from the mussel analysis in order to validate the environmental relevance of passive sampling. A good relation had previously been observed in field experiments in the Netherlands [(2)].

The central expert coordinating laboratory (The RIKZ/National Institute for Coastal and Marine Management, The Netherlands) prepared 600 silicone rubber membranes and distributed (n=18 per site) to the participating laboratories. Each silicone rubber sheet was solvent pre-extracted (Soxhlet extraction with ethyl acetate for 100 hours [(2)]) to minimise the possibility of pre-trial PCB/PAH contamination. The sheets were then spiked with 15 performance reference compounds (PRCs) covering a Log K_{ow} range from 3.5 (naphthalene-d_8) to ~8.0 (PCB 204) as described by Booij et al [(3)] (and summarised by Yates et al [(4)]). Briefly, 100 ml of methanol in an amber glass jar was spiked with known concentrations of the compounds of interest (See *Table 3.5*) and the silicone rubber sheets added. The glass jar was shaken for 2 hours on an orbital shaker at 200 rpm followed by addition of water to obtain 80% v/v methanol solution and

further shaken for 6 hours with a subsequent addition of water to obtain 50% v/v methanol solution. This was followed by shaking overnight at room temperature [4].

The level of depletion of PRCs during exposure acts as a measure of the sampling rate of the silicone rubber sheets during the deployment period. The silicone rubber sheets were stored in labelled bottles with lids lined with aluminium foil and stored in a freezer (-20^{o}C), except during transport and deployment. The PRCs used in this study and their Log $K_{sr,w}$ values [5] are outlined in *Table 3.5*.

For all stations, stainless steel frames and sampler holders were used for mounting of the silicone rubber membranes. Each sampler consisted of 6 sheets of silicone rubber (5.5 x 9 cm), with a total surface area of approximately 500 cm^2. Two samplers were mounted on the stainless steel frame (See *Fig. 3.5*) for each test site. A basket of mussels (*Mytilus edulis*) was secured (with screws and cable ties) at the frame base and the whole device was deployed at the test sites for approximately 6 weeks. The two Irish test sites were located in Dublin and Galway Bay (See Section 3.1). A third sampler acted as a reference for the determination of the initial concentrations of PRCs, while also acting as a storage and transport blank.

The exposure of silicone rubber membranes at the locations of interest allowed the passive sampling of the water phase. During the exposure time, compounds (including PCBs and PAHs) were transferred from the water phase to the silicone rubber, with the uptake rate being related to the freely dissolved concentrations of the contaminants in the water phase.

On retrieval, one replicate sampler (n=6 membranes) from each site was returned to the coordinating laboratory (RIKZ) for analysis, with the other replicate sample (n=6 membranes) and reference being analysed by the participating laboratory. Analysis for PCB and PAH was completed under subcontract by ERGO laboratories, Hamburg.

The analysis of the replicate samples by both the central and participating laboratories allowed for the trial to act as an analytical intercalibration exercise. Contaminants were extracted from the sheets in the laboratory and the extracts analysed to determine the amounts accumulated in the membranes during the deployment period. Performance reference compounds (PRCs) were used for *in situ* determination of sampling rate. Freely dissolved concentrations in the water phase were calculated by applying a model to determine the effective sampling rate. Procedures are fully documented in Section 3.8.2.

3.1 Site Descriptions and Selection

The two Irish test sites selected were Rinville Point (53 14.56N -8 58.376W), Galway Bay and the Northbank Lighthouse (NBL) (53 20.701N -6 10.587W), Dublin Bay.

Site 1: *Rinville Point, Galway Bay.*

While Galway Bay receives effluent from the city's municipal wastewater treatment plant (Mutton Island) as well as a variety of industrial discharges, pollution emitted from these sources is not to the same extent as is experienced in Dublin Bay. Vehicular and marine traffic are also a source of local pollution at both sites.

Rinville Point is an inlet of Galway Bay (See *Fig 3.1* and *Fig. 3.2*), which is more accustomed to boating activities of a recreational rather than commercial nature. The main regular boating activities in the Rinville Point area are those of a relatively small local sailing club.

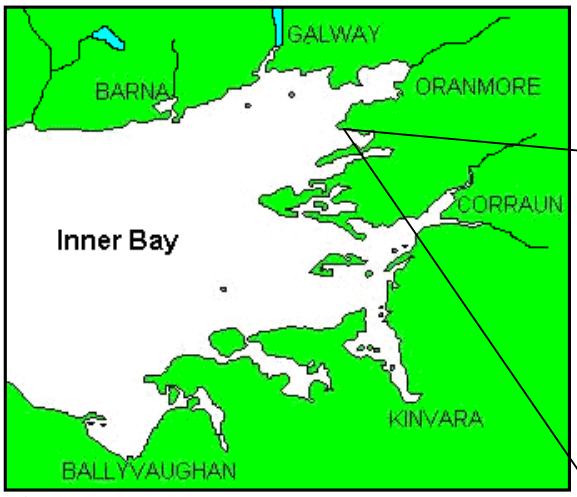

Figure 3.1: Inner Galway Bay. (Graphic reproduced from Anninou [6])

Figure 3.2: The buoy which the PS device was secured at Rinville Point, Galway Bay.

Three main rivers drain into the inner Bay area. The largest river, the Corrib enters the Bay at the north-eastern corner, while the Clarin and Kilcolgan rivers enter from the east. According to Fernandes [7] the water column in Galway Bay is partially or well mixed throughout the year. The direction of the winds (prevailing south-westerly) is the predominant driving force for mixing in the Bay and the tide to a lesser extent; other meteorological conditions, such as the amount of rainfall, can also influence the temperature and salinity distribution, as well as the water circulation [8].

According to the Central Statistics Office, the population of Galway city was about 72,500 in the year 2006 [9]. Prior to the installation of the Mutton Island sewage treatment plant, the city's raw sewage was pumped into the Bay via outfalls [10]. Since the plant was officially opened in May 2004 [11], the water quality in the Bay has improved significantly.

Site 2: *The Northbank Lighthouse (NBL), Dublin Bay.*

Dublin Bay is the largest industrialised Bay on the East coast of Ireland. In contrast to the limited pressures at Site 1, the NBL is positioned at the outskirts of a busy, heavily industrialised port (See *Fig. 3.3*).

The lighthouse stands on stilts within the Bull and East walls, an area within the outer river Liffey estuary which is also influenced by the inflow of the Dodder and Tolka rivers [(12)].

Dublin port is of major importance for international commerce. Influences of different marine traffic: commercial vessels such as oil tankers, container ships and freighters use the port to transport manufactured goods and raw materials, while passenger ferry ships and recreational boats are also major users. The combination of the highly industrialised nature of the area surrounding the port, the extent of marine traffic and population density mean that Dublin Bay is subject to chemical contamination from a variety of sources (See *Fig. 3.4*).

The NBL lies in close proximity to the Ringsend municipal wastewater treatment plant, which provides tertiary treatment for a population equivalent of 1.7 million [(12)].

Temperature and salinity data recorded at the NBL as part of the MATSIS (methods for the assessment of the tropic status of the Irish Sea) project clearly indicate seasonal variation. For example, the mean water temperature varied from 8.5 ^{o}C in November-December 2005 to 16.1 ^{o}C in summer 2006, while mean salinities varied from 30.9 PSU (practical salinity units) in October-December 2005 to 32.6 PSU in summer 2006 [(12)].

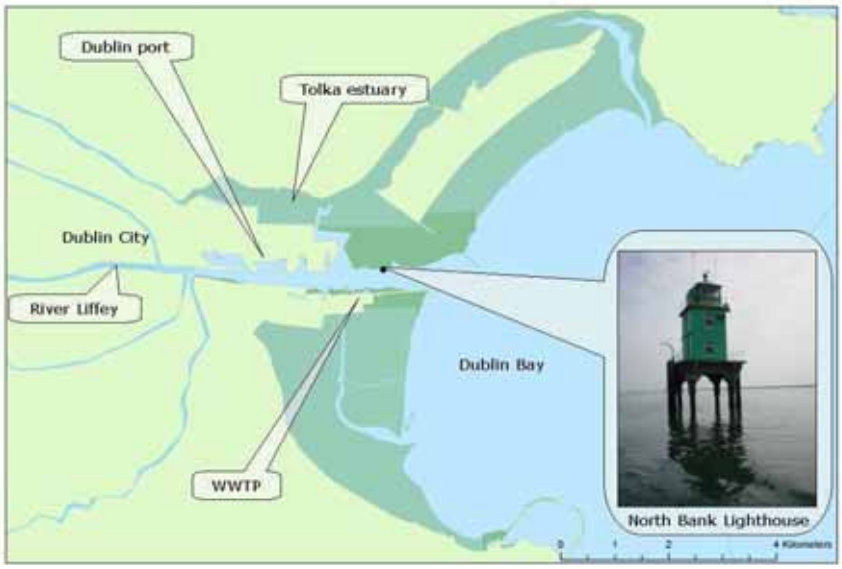

Figure 3.3: The North Bank lighthouse. (WWTP = Ringsend waste water treatment plant)

Figure 3.4: Site 2: The North Bank Lighthouse, Dublin Bay. (a) Marine traffic passes within close proximity to the Lighthouse, where the passive sampling device was secured. (b) Boating activities within the Port area. (c) Industrial Chimneys.

3.2 Mussel Collection and Equilibration

Mussel specimens (*Mytilus edulis*) of size 4-6cm were collected from the Rinville shoreline, in the vicinity of the passive sampling trial location, (GPS: N53 14.696 8° 58.475W) on the 11th of October, 2006. They were wrapped in netting with seaweed and stored in saltwater for 48hrs. Depurated mussels were then transported to Dublin Bay and allowed to equilibrate at the Northbank Lighthouse (Dublin) for 26 days prior to deployment with the PS membranes.

3.3 Sampler Assembly

The PS holders were attached to the sampler frame and six silicone rubber sheets were secured to each holder. Equilibrated mussels were placed into the basket and attached to the bottom of the sampling frame (See *Fig. 3.5*). The frame was covered with mesh to minimise accidental damage/predation/fouling (See *Fig. 3.6*).

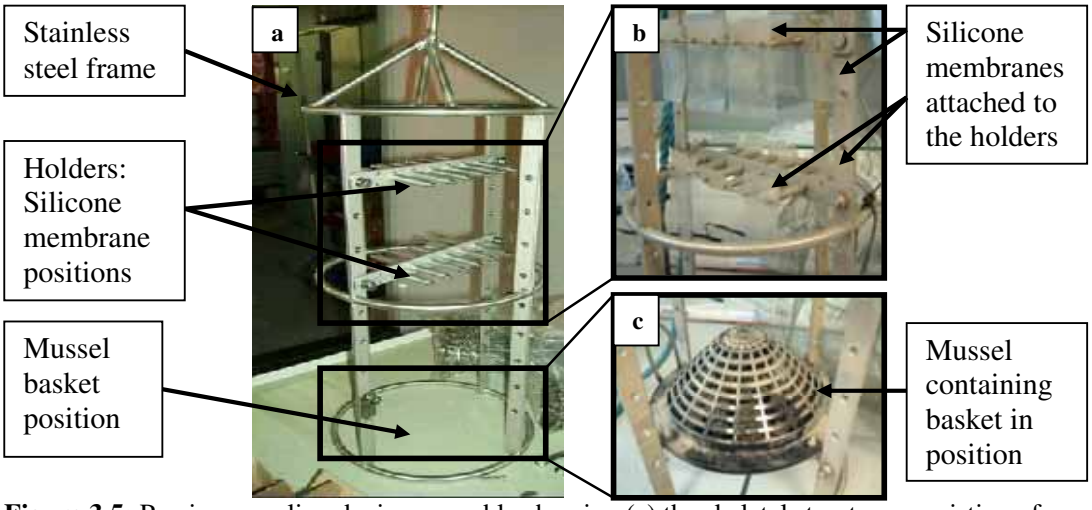

Figure 3.5: Passive sampling device assembly showing (a) the skeletal structure consisting of the stainless steel frame and holders, (b) the attached silicone rubber membranes and (c) the basket of mussels secured to the base of the frame.

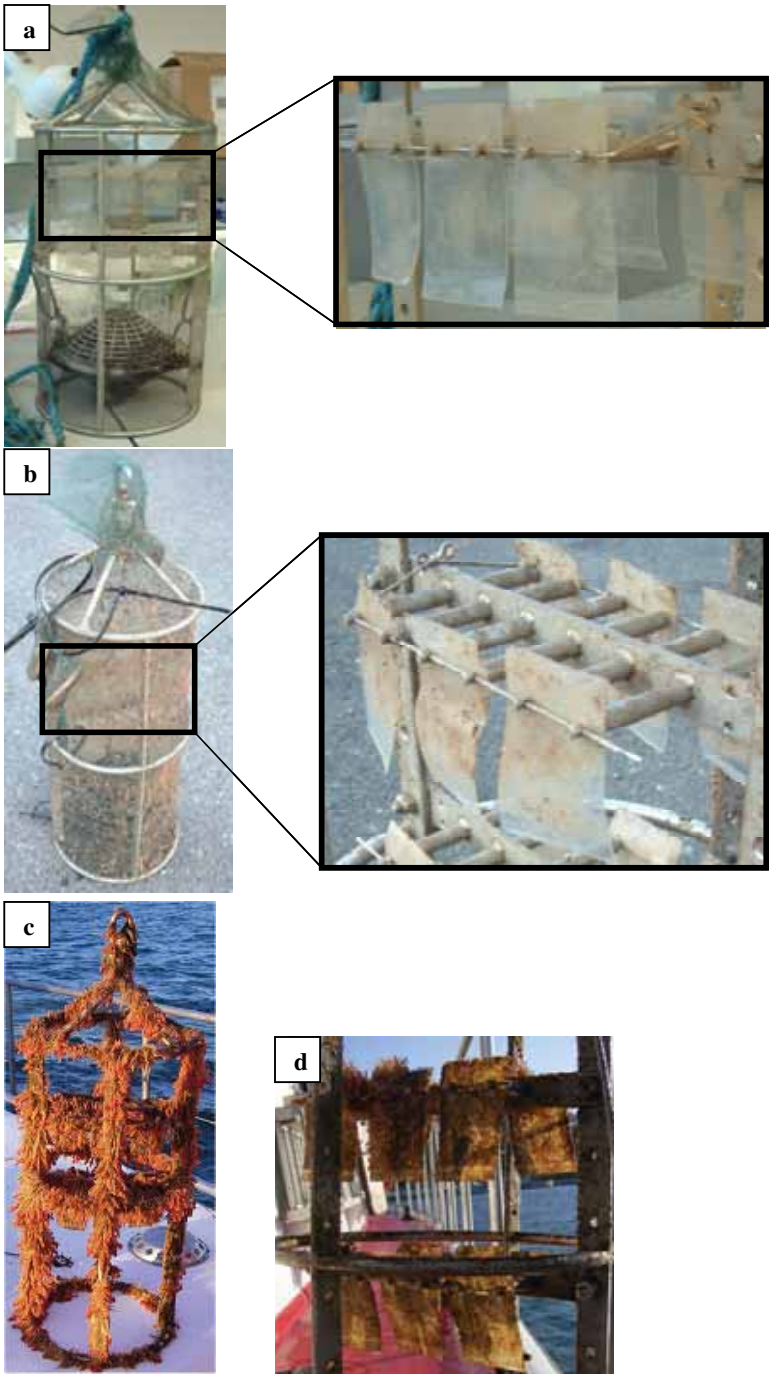

Figure 3.6: The mesh covered passive sampling devices recovered from (a) Galway and (b) Dublin experienced different degrees of biofouling. The level of biofouling experienced in Ireland was minor when compared to (c) the passive sampling frame and (d) membranes recovered from other PSTS sites.

3.4 Sampler Deployment and Retrieval

The steel devices together with silicone rubber sheets and mussels were secured to permanent moorings at Rinville Point, Galway Bay (7th November, 2006) and the Northbank Lighthouse (NBL), Dublin Bay (6th November, 2006). At the end of the exposure period (6 weeks), both samplers were retrieved and brought ashore intact between the 19th and 20th December, 2006.

3.5 Sampler Disassembly

The mesh was removed from the sampler frame, the silicone rubber sheets detached and cleaned. Cleaning involved gently wiping the sheets with damp (deionised water) tissue, to remove the biofilm (See *Fig. 3.7*). The sheets were then put into the original glass jars in which they arrived and stored in the freezer. Size classed mussels (size range 4-6cm) were recovered and depurated overnight at 4-6 ^{o}C. The mussels were measured (*Table 4.3*) and the soft body tissue removed from the shells. The flesh was pooled, homogenised and stored in solvent washed jars prior to analysis.

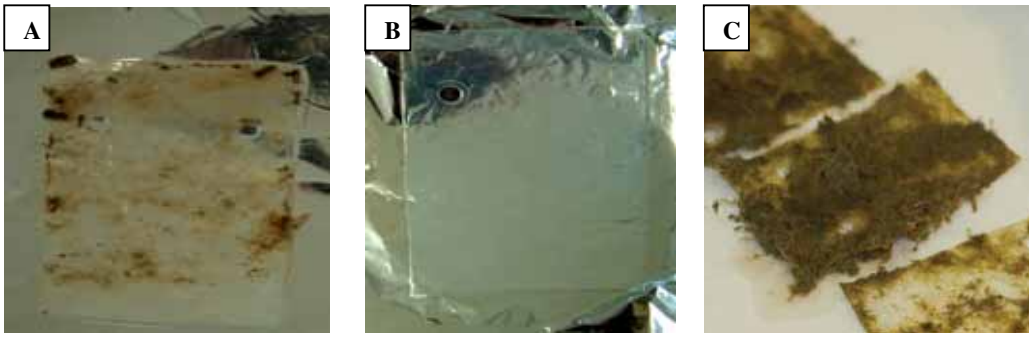

Figure 3.7: Exposed silicone rubber membrane from Dublin Bay (a) before and (b) after cleaning. The Dublin membrane is only slightly biofouled when compared to (c) membranes recovered from another PSTS participant's site.

3.6 Sample Analysis

One half of each set of deployed sheets i.e. six sheets from each site, were then subcontracted to the ERGO laboratory in Hamburg for the analysis of environmentally derived PCBs and PAHs and for the remaining PRCs. Contaminants in mussel and spot water samples were additionally analysed by ERGO. The second half of the PS membranes were sent back to the central reference laboratory (RIKZ laboratory, Netherlands) in order for the degree of analytical variation between laboratories to be estimated.

The data obtained from ERGO for all sample media, i.e. water, mussels and PS membranes are from here on referred to as the Marine Institute (MI) results and the RIKZ data referred to as Reference (Ref) results.

A number of biological parameters were measured in the transplanted mussels. These are further discussed below.

3.6.1 Measurement of a Species Condition Index

In order to assess whether transplantation adversely affected test species, a simple surrogate condition index (CI) was derived by calculating the individual mean whole-body tissue dry weight for each test species throughout the transplantation study. This average weight was further divided by the mean organism length (mm) to derive a proxy indicator of condition that reduced the inherent variability associated with differences in growth of individual locations. The resulting unitless figure was then multiplied by 1000, in an attempt to produce a more manageable number.

3.6.2 Determination of Lipid Content in Marine Biota Tissue

Exposure of aquatic organisms to pollution can translate into an impairment of lipid metabolism, e.g., changes in subclasses of lipids, membrane fluidity and transport of lipids and in an increase in lipid content [13]. Total Lipid determination was completed by the internationally recognised "Smedes" method [14, 15]. The Smedes tri-phasic solvent and water extraction is suitable for the determination of total lipid content of marine samples. Briefly, a total of 16 ml iso-propanol and 20 ml cyclohexane were added to an accurately weighed sub-sample of the defrosted and homogenized sample. The sample is then homogenised and centrifuged. The organic layer is then carefully removed. Water added and the procedure repeated and organic layers pooled. The sample is then evaporated to dryness and the lipid content determined gravimetrically. A detailed description of this method is provided in Appendix 2.

3.6.3 Determination of Moisture Content in Marine Biota Tissue

The method described herein is based on the AOAC Internatioal's Official Method for Moisture in Meat [16]. This oven-based method is used to quantify the moisture content in marine biota (i.e. shellfish), whereby the moisture content is the amount of moisture in a material determined under prescribed conditions and expressed as a percentage of the weight of the moist specimen.

Briefly, the mussel sample was homogenised. The weight of an aluminium dish was recorded (A) and tarred. An approximate 1g portion of the fish homogenate was weighed into the pre-weighed aluminium dish, and the exact weight of moist tissue recorded (S_w). The sample was then oven dried at 104 °C ± 2 °C for ≥16 hours. On removal from the oven, the tissue sample was stored in a desiccator to allow it equilibrate to room temperature. The aluminium dish and dried sample were weighed and the weight recorded (B). The moisture content is calculated and expressed as a percentage of the weight of the moist specimen as follows:

$$\text{Moisture Content (\%)} = \left[\frac{S_w - S_d}{S_w}\right] x100 \qquad \textit{Eqn. 3.1}$$

Where:

A = Weight of Container

B = Weight of Container + Dry Sample

S_w = Weight of Wet Sample.

S_d = Weight of Dry Sample. S_d = B - A

3.6.4 Analysis of PCBs/PAHs and PRC Compounds

The analysis of individual matrices for both analyte groups of interest and for PRCs (in the case of passive sampling membranes) was completed in a one or two stage process. Depending on the sample matrix, this involved;

i) Stage I (mussels, passive sampling membranes and spot water samples): the spiking of matrices with appropriate labelled/deuterated internal standards followed by extraction, clean-up and GC-MS analysis.

ii) Stage II (passive sampling membranes only): the addition of known volumes of an external standard to the GC-MS samples in i) above was completed. This enabled peak area normalization between samples to be completed, enabling PRC dissipation to be estimated thus allowing for the determination of the sampling rate (R_S) to be completed. These processes are further described below.

3.6.4.1 Stage I analysis:

3.6.4.1.1 PCB analysis in mussels, spot water and passive sampling membranes

Prior to extraction ^{13}C-labelled internal standards (which differed from those used as PRC compounds) were added to the samples (*Table 3.1*). The samples (including blank PS membranes) were then extracted/solved with appropriate solvents for ultratrace-analyses (e.g. nanograde) by using a solid/lipid extraction, followed by the clean up which was performed on a multicolumn system (involving carbon-on-glassfibre). Analytical measurement was completed by means of high resolution gas chromatography and high resolution mass spectrometry (HRGC/HRMS) with VG-AutoSpec and/or Finnigan MAT 95 XL using a DB-5 capillary column. For each of the Marker PCBs, 2 isotope masses were measured. Quantification and recovery correction (Section 3.6.5) was completed utilising the spiked ^{13}C-labelled internal standards. Resultant concentrations were then utilised for data assessment purposes (Chapter 4).

All matrices were analysed for a total of fifty-one PCBs, these being split into 3 smaller, sub- groups namely;

- The twelve World Health Organisation (WHO) PCBs (PCB 77,81,126,169,105,114,118*,123,156,157,167 and189),
- The seven Marker PCBs (PCB 28,52,101,138,153,180 and 118*)
- Thirty-three other PCBs (PCB 18, 31, 33, 41, 44, 47, 49, 51, 56/60, 61, 66, 74, 87,99,110, 128, 129, 141, 149, 151, 170, 183, 185, 187, 191, 193, 194, 201, 202, 203, 206, 208, 209).

PCB 118 falls into two of the named categories, being both a WHO and marker PCB, and as such is denoted by an * in the above lists. For the purpose of this project, PCB 118 results are treated under both categories, thus appearing twice in the results table and subsequent graphs.

3.6.4.1.2 PAH analysis in mussels and passive sampling membranes

Prior to analysis, labelled internal standards (which differed from those used as PRC compounds) were added to the passive sampling membranes, water and mussel samples (*Table 3.1*). The samples were then extracted with acetone by using a liquid/solid extraction, followed by a liquid/liquid seperation. Clean up was performed on a multicolumn (Alumina silica) system. STAGE I measurement was completed by high resolution gas chromatography coupled to mass spectrometry (HRGC/MS). Quantification and recovery correction (Section 3.6.5) was completed utilising the spiked labelled standards. Resultant concentrations were then utilised for data assessment purposes as outlined in Chapter 4.

All sample matrices were analysed for a total of twenty-one PAHs, these being divided into two groups, primarily being based on;

- The sixteen United States Environmental Protection Agency (US EPA) PAHs (naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo[a]anthracene, chrysene(*), benzo[b]fluoranthene(**), benzo[k]fluoranthene(**), benzo[a]pyrene, indeno[1,2,3-c,d]pyrene, benzo[g,h,i]perylene and dibenzo[a,h]anthracene)
- Six others; (benzo[b]naphtho [2,1-d] thiophene, benzo[c]phenanthrene, benzo[g,h,i]fluoranthene, benzo[e]pyrene, anthanthrene, coronene).

Note: PAH results reported deviate slightly from the US EPA list above in that:

(*) chrysene was measured as a combination of chrysene and triphenylene.

(**) benzo[b]fluoranthene and benzo[k]fluoranthene were not measured individually, but as a combination of three PAH compounds, i.e. benzo[b]fluoranthene, benzo[j]fluoranthene and benzo[k]fluoranthene, resulting in the final concentration being represented as benzo[b+j+k]fluoranthene.

Table 3.1: Labelled Internal Standards (IS) added prior to extraction of the water, mussel and PS membrane samples from both the Galway and Dublin test sites

^{13}C-UL PCBs			Labelled PAHs		
WHO		Marker			
77	118	28	Phenanthrene-d_{10}	Indeno[1,2,3-cd]pyrene-d_{12}	Acenaphthylene-d_8*
81	123	52	Anthracene-d_{10}	Benzo[ghi]perylene-d_{12}	Pyrene-d_{10}*
126	156	101	Fluoranthene-d_{10}	Coronene-d_{12}	Benzo[a]pyrene-d_{12}*
169	157	138	Benzo[a]anthracene-d_{12}	Benzo[b]fluoranthene-d_{12}	Dibenz[a,h]anthracene-d_{14}*
105	167	153	Chrysene /	Benzo[b]naphthol	
114	189	180	Triphenylene-d_{12}	[2,1]thiophene-d_{10}	Benzo[k]fluoranthene-d_{12}*

All other PCB congeners (other than WHO and Marker PCBs) were analysed using the ^{13}C-UL PCBs mentioned above. The same PCB internal standards were added to all sample media i.e. water, mussels and PS membranes. However, different PAH internal standards were used for water and mussel samples than for the PS membranes. All the PAH IS (exception benzo[k]fluoranthene-d_{12}*) were used for water and mussels while those used for the PS membrane are denoted by *.

3.6.4.2 Stage II analysis

Prior to GC-MS analysis a constant weight of an external standard was added to each GC-MS vial, for use in Stage II measurements only. The external standard was then used for the purposes of normalisation of peak areas, this being completed in a stepwise process as follows,

- The peak areas of the external standard and each of the PRCs in each of the GC-MS extracts was recorded.
- Normalisation ratios were calculated for the peak area of each of the PRCs relative to the peak area of the external standard (i.e. External standard peak area/PRC x peak area).
- The normalisation ratio determined in the T=0 PS blank was then deemed to correspond to a situation where no PRC dissipation had taken place.
- Normalisation ratios on Tend passive sampling extracts were then calculated and compared to those in the T=0 extract.

Where dissipation of PRCs was observed at the end of the exposure period, this was reflected in an increase in the external standard: PRC ratio. Where no dissipation occurred, the ratio at the end of the exposure period would have been the same as the blank. In the case of high molecular weight compounds which show limited dissipation, the external standard: PRC ratio in the membranes at the end of the period was determined to be similar to that of the blank. Finally the extent of PRC dissipation (normalisation ratio) in the Tend PS membranes was calculated relative to the T=0 blank. It should be noted that while the reference laboratory completed analysis using a different protocol the derived sampling rates at both sites were relatively similar, thus validating the documented approach.

3.6.5 Quality Assurance of Analysis

Quality Control (QC) information from analyses carried out by the Reference laboratory is not currently available, as the final report for the overall ICES study is pending. The QC discussed herein relates to the Marine Institute (MI) analysis of samples, detailing the percentage recoveries of analytes and the calculation of a |z| score for lipid determination in the mussel samples.

3.6.5.1 Percentage Recovery of Analytes

Table 3.2 (PCBs) and *Table 3.3* (PAHs) provide the percentage recoveries of various compounds analysed by the MI during the course of this study. In summary, although the percentage recoveries are low for many compounds in the various matrices, the final MI contaminant concentrations (corrected for the percentage recoveries outlined in this Section) are similar to those reported by the Reference laboratory (See Section 4.2.4).

Table 3.2: Percentage Recoveries of various PCB compounds analysed in the Spot water samples, Passive sampling membranes and mussel tissues taken from the Galway and Dublin sites during the course of this study

Sample	Spot		Passive Sampler			Mussels				
Location	Galway	Dublin	Galway	Dublin	Blank	Galway		Dublin		
						T(start)	T(end)	T(start)	T(end)	Native NBL
PCB 28	77.0	120	79.0	83.5	71.9	76	80.9	75.1	78	71.9
PCB 52	85.5	141	81.0	90.0	81.1	81.7	92.7	89.1	93.5	86.3
PCB 77	84.2	80.7	76.1	84.8	81.7	64.7	81.4	81.2	85.1	79.7
PCB 81	81.6	86.8	73.8	82.3	78.8	63.0	79.1	79.8	81.7	77.8
PCB 101	94.7	153	83.0	92.4	89.7	92.2	113	115	127	110
PCB 105	86.2	86.9	81.3	86.8	81.2	75.2	79.6	79.0	84.7	84.5
PCB 114	83.3	78.3	79.4	83.8	78.5	72.2	81.4	76.9	82.9	83.5
PCB 118	82.2	133	80.3	84.4	78.1	73.2	78.9	78.8	81.4	79.8
PCB 123	83.7	78.7	78.2	83.2	79.1	72.8	77.6	76.7	83.7	79.7
PCB 126	76.7	91.5	76.1	87.0	82.8	56.2	77.7	74.7	79.9	75.8
PCB 138	85.7	136	85.0	96.0	84.9	78.6	85.2	85.6	93.6	89.2
PCB 153	86.3	135	81.0	92.8	82.7	76.7	84.5	84.9	92.3	88.6
PCB 156	84.7	145	80.4	90.7	80.9	76.0	82.7	85.2	88.6	88.3
PCB 157	82.3	71.3	81.5	91.4	79.9	73.6	81.3	85.6	87.3	83.1
PCB 167	81.2	86.8	81.2	93	81.9	74.9	82.2	83.2	86.6	83.9
PCB 169	76.7	77.8	73.6	82.6	82.0	58.5	73.2	75.1	77.3	75.1
PCB 180	82.0	122	73.0	90.0	73.2	76.5	80.9	86.7	93.6	84.4
PCB 189	121	120	122	134	121	105	118	108	115	112
PCB 209	79.5	63.8	59.0	88.0	61.1	76.5	70.8	77.0	83.9	82.8

Table 3.3: Percentage Recoveries of various PAH compounds analysed in the Spot water samples, Passive sampling membranes and mussel tissues taken from the Galway and Dublin sites during the course of this study

Sample Location	Spot		Passive Sampler			Mussels				
						Galway		Dublin		
	Galway	Dublin	Galway	Dublin	Blank	T(start)	T(end)	T(start)	T(end)	Native NBL
Ace	55.3	80.5	24.3	21.1	11.4	22.1	15.6	12.8	29.6	5.29
P	23.7	50.2				30.6	17.2	17.0	33.0	6.38
A	15.6	38.4				19.5	8.60	10.5	16.7	4.50
Fl	27.6	59.2				43.3	31.1	29.0	58.5	9.83
Py	28.7	55.7	64.9	60.8	46.2	42.9	32.4	26.5	54.4	8.07
BbN	27.2	52.3				42.0	32.7	25.1	45.9	6.88
BaA	26.8	55.1				44.2	35.0	38.0	51.6	15.2
C-T	30.5	46.8				46.8	43.9	36.4	52.9	11.8
BbjkF	22.6	48.2	57.6	66.5	58.9	52.8	42.3	33.6	38.9	23.5
BaP	20.7	41.6	83.4	66.6	81.8	35.0	28.0	32.4	30.5	19.0
IP	17.8	46.0				41.6	35.0	32.6	37.0	22.7
BghiP	19.3	40.8				43.4	37.5	31.8	39.3	20.2
DahA	17.7	49.4	69.7	67.0	73.2	44.8	39.9	32.5	38.5	26.2
Co	25.6	42.5				62.4	65.8	30.9	95.9	42.9

Note: Ace: Acenaphthylene; P: Phenanthrene; A: Anthracene; Fl: Fluoranthene; Py: Pyrene; BbN: Benzo[b]naphtho [2,1-d] thiophene; BaP: Benzo[a]anthracene; C-T: Chrysene – Triphenylene; BbjkF: Benzo[b+j+k]fluoranthene; BaP: Benzo[a]pyrene; IP: Indeno[1,2,3-cd]pyrene; BghiP: Benzo[ghi]perylene; DahA: Dibenz[ah]anthracene; Co: Coronene

3.6.5.1.1 Percentage Recovery of PCB Compounds

The percentage recoveries for PCBs in the Spot water samples range from 76.7-121 % (mean 84.8 %) for Galway and 63.8-153 % (mean 110 %) for Dublin. The recoveries for PCB 189 are consistently highest throughout all samples (spot water, PS membranes and mussel samples), except for the Dublin Spot sample.

Recoveries for PCBs in the Dublin membrane are consistently higher than those in the Galway and blank membranes, with percentage recoveries ranging from 82.3-134 % (mean 90.4 %) for Dublin, 59.0-122 % (mean 79.6 %) for Galway and 61.1-121 % (mean 80.8 %) for the blank.

The percentage recoveries for PCBs in the mussel samples range from 56.2-105 % (mean 75.9 %) for Galway T(start), 70.8-118 % (mean 84.8 %) for Galway T(end), 74.7-108 % (mean 84.9 %) for Dublin T(start), 77.3-115 % (mean 90.3 %) for Dublin T(end) and 71.9-112 % (mean 85.6 %) for the Native NBL sample.

3.6.5.1.2 Percentage Recovery of PAH Compounds

The percentage recoveries for PAHs in the Spot water samples range from 15.6-55.3 % (mean 25.6 %) for Galway and 38.4-80.5 % (mean 50.5 %) for Dublin, with anthracene having the lowest percentage recoveries and acenaphthylene having the highest in both.

Of the five PAH compounds for which percentage recoveries are reported for the passive samplers (*Table 3.3*), the recoveries for four of the PAHs in the Galway membrane are higher than those in the Dublin membrane (exception benzo[b+j+k]fluoranthene). Percentage recoveries range from 24.3-83.4 % (mean 60.0 %) for Galway, 21.1-67.0 % (mean 56.4 %) for Dublin and 11.4-81.8 % (mean 54.3 %) for the Blank. Acenaphthylene has the lowest percentage recovery in all membrane samples.

The percentage recoveries for PAHs in the mussel samples range from 19.5-62.4 % (mean 40.8 %) for Galway T(start), 8.6-65.8 % (mean 33.2 %) for Galway T(end), 10.5-38.0 % (mean 27.8 %) for Dublin T(start), 16.7-95.9 % (mean 44.5 %) for Dublin T(end) and 4.5-42.9 % (mean 15.9 %) for the Native NBL sample. Anthracene consistently has the lowest percentage recovery in the mussel samples, with coronene having the highest percentage recovery in four of the five samples (exception Dublin T(start) sample.

Overall, the percentage recoveries reported for the PCB compounds (*Table 3.2*) are greater than those reported for the PAH compounds (*Table 3.3*). The final contaminant concentrations, as reported in the summary tables (*Tables 4.13 - 4.16, 4.18*), have been corrected accordingly for the percentage recoveries outlined in this Section.

3.6.5.2 |Z| score for Lipid Determination

Quality assurance for the lipid determination carried out by the MI on the mussel samples taken during this study was provided by means of analyzing a QUASIMEME mussel tissue in conjunction with the test samples. The method for lipid content determination is briefly described in Section 3.6.2, with a more detailed description provided in Appendix 2.

The |Z| score determined for the QUASIMEME (QPH033BT.1) used during this study is shown below. |Z| scores are calculated by QUASIMEME according to the formula:

$$Z = \left[\frac{(Calculated\%Lipid) - (QCAssigned\%Lipid)}{(QCAssigned\%Lipid)x\left(\frac{QCAssignedError\%}{100}\right)} \right]$$

The Calculation below is for the extraction of lipid from QPH033BT.1:

Calculated lipid content (%): 2.321
Assigned lipid content (%): 2.219
Assigned error (%): 14.75
|Z| = (2.321-2.219)/((2.219x(14.75/100))
|Z| = 0.102/0.327
|Z| = 0.312

The |Z| score determined for QPH033BT.1 ensures the reliability of the test mussel lipid content data (*Table 4.3*), as the |Z| score (0.312) is well within the acceptable range of <2.

3.7 Data Assessment Methodologies

In order for data from individual matrices to be comparable a number of conversion methodologies were required. These included conversion of data from lipid weight to wet weight and additionally on how to treat analytical data lower than the limit of quantification (LoQ) for the sub-contracted laboratory. These (and working examples) are further discussed below.

3.7.1 Converting between lipid-wet-dry weight basis

The normalisation of contaminant concentrations in organisms by the lipid content of the tissues is based on the fact that accumulation of hydrophobic compounds is governed by their affinity with lipids [(17)]. In order to convert the concentration data from lipid weight to wet weight, and furthermore, dry weight, the following calculations were performed (*Table 3.4*). The concentration of PCB 18 in the native NBL mussel sample has been used to demonstrate the calculations involved.

Table 3.4: Conversion measures taken to convert the PCB 18 mussel concentration data detected in the native NBL mussel sample from a lipid to wet to dry weight basis, and finally to a lipid normalised dry weight basis

lipid to wet wgt		wet to dry wgt		dry to lipid normalised dry wgt	
lipid wgt	5.10µg/kg	**wet wgt**	0.103 µg/kg	**dry wgt**	0.469 µg/kg
lipid content	2.02%.	**average dry wgt**	22%	**lipid content**	2.02%
calculation	(5.10/100)*2.02	**calculation**	(0.103/22)*100	**calculation**	(0.496/2.02)
wet wgt conc	0.103 µg/kg	**dry wgt conc**	0.469 µg/kg	**lipid normalised dry wgt conc**	0.232 µg/kg

3.7.2 Treatment of Values less than the Limit of Quantification (LoQ)

For each analytical parameter a limit of quantification (LoQ) was derived, this being deemed as the concentration above which the laboratory state that suitable statistical and quality control are available to enable quantification at the stated level. Compounds which have not been detected in a sample i.e. the concentration fell below the LoQ, are noted in the results tables (*Tables 4.13 - 4.16, 4.18*), by a less than (<) symbol.

In such cases the LoQ value was selected as being the “upperbound” level at which the compound may be present in the particular sample. Where such values were obtained the <LoQ concentration was carried through appropriate calculations e.g. PAH data converted from lipid to wet to dry weight. All <LoQ values are documented in relevant tables however for the purposes of graphical representation, these <LoQ values for compounds which are not detected were omitted.

Finally, as concentration ranges may span orders of magnitude, it was often necessary for graphical purposes to transform analytical data, this being completed by Log (x+1) conversions. These transformed data were not used for assessment purposes. Briefly, the Log (x+1) conversions are a data transformation process used solely for graphical purposes. The plus one is used because in instances where analytical data are <1, carrying out a Log results in a negative value. Therefore the addition of 1 beforehand ensures the generation of positive integers for graphical purposes. The Log (x+1) data are used only for plotting purposes to enable the representation of high and low data on the same graph. This data was not used in carrying out the comparison of results.

3.8 Methods to Determine Dissolved Pollutant Water Concentrations

This project is primarily concerned with assessing the applicability of passive sampling methodologies for the measurement of dissolved PCBs and PAHs in the water column. Water samples provide an indication of spot sampling techniques while the mussels provide an equilibrium approach to analysis. Concurrent comparison with the silicone rubber membranes allows assessment of the performance of the membranes compared to other methodologies.

In order to compare and contrast the contaminant data obtained from the various media, (i.e. spot water sample, PS and mussels), the data must be expressed on a comparable basis. Three methodologies were utilised in order to convert analytical data to comparable basis i.e. PCB (pg/l) and PAH (ng/l). Thus dissolved water concentrations (C_w) were determined for both Galway and Dublin sites using the following:

3.8.1 Direct analysis of the water spot samples.

3.8.2 Passive sampler derived C_w, using optimised sampling rates (R_S).

Approaches to complete these are further discussed below.

3.8.1 Direct Analysis of the Water Spot Samples

Direct analysis of the concentrations of freely dissolved contaminants was performed on unfiltered spot water samples from Galway and Dublin. Analyte quantification methodologies are reported in Section 3.6. For these analyses, the data are reported in an appropriate format (pg/l PCBs and ng/l PAH).

3.8.2 Passive Sampler Derived C_w, using Optimised Sampling Rates (R_S)

In order to ultimately yield an estimate of the freely dissolved aqueous-phase concentrations from the passive sampling membranes, a number of data conversions and calculations are required. This is achieved through the following stepwise process:

3.8.2.1 Assessment/selection of appropriate PRCs.

3.8.2.2 Calculation of the Passive Sampler Sampling Rate (R_S).

3.8.2.3 Conversion of PS membrane data into water concentrations.

These are further discussed below.

3.8.2.1 Assessment/Selection of Appropriate PRCs

The concept of the use of PRCs is previously described (Section 2.6), however in summary, the sampling rate (R_S) can be simply described as the equivalent spot sample water volume that is sampled during a given time period. The R_S values for the two test locations were determined using the PRC dissipation information obtained from the field studies. The percentage recovery of spiked PRCs in the PS membranes at the end of the exposure period for both sites are detailed in *Table 3.5*.

Table 3.5: The PRC compounds utilised during the PSTS, their silicone rubber-water partition co-efficients (Log $K_{sr,w}$) [5] and the percentage of each individual PRC remaining in the PS membranes at both Galway and Dublin after the exposure experiment

		% PRC remaining					% PRC remaining		
PRC	**Log $K_{sr,w}$**	**Galway**	**Dublin**	**Blank**	**PRC**	**Log $K_{sr,w}$**	**Galway**	**Dublin**	**Blank**
PCB 10	4.52	66.1	116	100	**PCB 204**	7.61	108	108	100
PCB 14	5.07	103	113	100	**Naphthalene-d_8**	2.99	0.00	0.00	100
PCB 21	5.37	102	113	100	**Fluorene-d_{10}**	3.70	3.5.0	36.3	100
PCB 30	5.21	106	117	100	**Phenanthrene-d_{10}**	4.01	10.5	68.1	100
PCB 50	5.67	109	126	100	**Fluoranthene-d_{10}**	4.52	31.6	114	100
PCB 55	5.94	104	102	100	**Chrysene-d_{12}**	5.16	47.3	132	100
PCB 78	5.99	62.8	58.4	100	**Benzo[e]pyrene-d_{12}**	5.55	48.2	120	100
PCB 104	6.16	108	107	100	**Perylene-d_{12}**	5.40	41.9	116	100
PCB 145	6.64	112	110	100	**Coronene=d_{12}**	6.39	45.0	104	100

Note: The Blank PS membrane was unexposed and retains its 100% PRC composition.

On the basis of examination of the site specific datasets, literature comparison and protocols as agreed within the wider international study guidelines, a number of PRCs (PCB 145 and PCB 204), were selected as being suitable internal standards for use in order to complete the process of the estimation of the "common sampling rate" R_S. According to Yates (Personal communication), the PRCs mentioned above were chosen as they are not depleted during the 6 week exposure period.

3.8.2.2 Calculation of the Passive Sampler Sampling Rate (R_S)

Estimation of the "common" R_S is effectively a measure of the degree of similarity between the measured dissipation curve and the calculated dissipation curve, determined using the percentage of PRCs in the original membranes (100 %) and the percentage remaining in the membranes after the exposure study. (See "example calculations" below for more detail).

For further explanation purposes the scatterplot (*Fig. 3.8*) reports the measured dissipation curve (Ne/No) and the calculated dissipation curve (Calc Ne/No) as a function of the Log $K_{sr,w}$ (membrane partition co-efficient) for the compound of interest. Columns "A" and "B" in *Table 3.6* report the dataset utilised in the generation of *Fig. 3.8(a).*

The observed difference between the values for Ne/No and the Calc Ne/No is essentially a function of the sampling rate of the membrane at the particular location. In order to generate the "best fit S-curve" between Ne/No and Calc Ne/No. i.e. to minimize the difference between the individual curves, it is necessary to identify the best sampling rate for the site.

The resulting 'S' shaped curve moves to the right or left as the R_S values change i.e. in higher flow areas (Galway), the curve will be shifted to the right, and at lower flows (Dublin) this curve will shift to the left. In order to complete this process it is necessary to complete a number of stages.

i) Quantification of differences between individual contaminant Ne/No and Calc Ne/No

A mechanism to quantify the degree of difference between Ne/No and Calc Ne/No was thus required. For this study a measure of the "similarity" between observations was calculated as follows;

$$\textit{Difference } \Delta = (\text{Ne/No minus Calc Ne/No}) \qquad \textbf{\textit{Eqn. 3.2}}$$

The measured differences (Δ) between individual contaminant observations are reported in *Table 3.6* Column "C".

ii) Quantification of the combined contaminant differences (ΣΔ).

In i) above the individual differences (Δ) were measured, however in order to best describe the performance/sampling rate of the membrane for a range of contaminants, it was necessary to derive an expression that combines the individual Δ observations.

$$\textit{Sum of Differences } (\Sigma\Delta) = (\Delta \text{ PCBn} + \Delta \text{ PAHn}) \qquad \textbf{\textit{Eqn. 3.3}}$$

Where: n represents 10 individual PCB PRCs and 8 individual PAH PRCs.

iii) Determination of the "Optimal" R_S

In order to minimize the sum of the differences ΣΔ (i.e. to find a value for ΣΔ as close to zero as possible), it is necessary to find the "optimal" R_S value. Finding this optimal R_S value can be completed manually by entering a range of R_S values (e.g. 0 to 100) into the *Eqn. 3.3*, or by using the Excel "solver" add-on. In this latter option a macro was run to derive the "optimal" R_S value thus ensuring that ΣΔ came as close to zero as possible for the current dataset. This is completed initially, including all PRC values.

However, in order to determine a more accurate R_S value, a number of PRC values must be excluded from the resultant table (*Table 3.6*) and curve (*Fig. 3.8(a)*). No standard selection criteria for PRC exclusion was available to participants in the PSTS exercise. Thus during the course of this work, PRCs were excluded primarily on the basis of personal communication with the other participants in the PSTS exercise (namely K. Yates [18]) and with the overall project co-ordinator (F. Smedes [19]). The basis for excluding values include: the value in Column "A" being greater than 1.00 or equal to 0, outliers (visible from the PRC dissipation curve plots) and values in Column "C" which fall outside the range of +/- 0.1. Such compounds have been selected as "excluded" in *Table 3.6* (beige column) and *Fig. 3.8(a)* (indicated by an "x"). Following the exclusion of PRCs, the solver function was rerun on the dataset to again obtain a value as close to zero as possible i.e. to obtain the optimised R_S value.

In the case of the Galway dataset the ΣΔ = 0.0204 resulted in a sampling rate R_S of 8.48 litres per day (l/d) (See *Table 3.6*). The Dublin sampling rate was determined in a similar manner, resulting in a R_S of 2.38 l/d. The "S" shaped PRC dissipation curves for Rinville Point, Galway Bay and the NBL, Dublin Bay are presented in *Fig. 3.8*.

Table 3.6: Determination of the Galway PS sampling rate (R_S) with a 42 day exposure period and 20g membrane weight. R_S value of 8.48 litres per day (l/d).

				R_S (l/d):	8.48	Optimizer	ΣΔ = 0.0204
	% PRC remaining				A	B	C
PRC	Galway	Blank	Use/ exclude	$K_{sr,w}$	Ne/No	calc Ne/No	Δ
PCB10	66.1	100		4.52	0.603	0.584	0.019
PCB14	102.6	100		5.07	0.937	0.859	0.077
PCB21	101.7	100		5.37	0.928	0.927	0.001
PCB30	106.1	100		5.21	0.969	0.896	0.072
PCB50	109.4	100		5.67	0.999	0.963	0.036
PCB78	62.8	100	Excluded	5.99	0.573	0.982	
PCB55	104.2	100		5.94	0.951	0.980	-0.029
PCB104	108.1	100		6.16	0.987	0.988	-0.001
PCB145	111.5	100	Excluded	6.64	1.018	0.996	
PCB204	107.6	100		7.61	0.982	1.000	-0.017
NAPxD8	0	100	Excluded	2.99	0.000	0.000	
FLExD10	3.5	100		3.7	0.032	0.029	0.003
PAxD10	10.5	100		4.01	0.096	0.176	-0.080
FluxD10	31.6	100	Excluded	4.52	0.288	0.584	
ChrxD12	47.3	100	Excluded	5.16	0.432	0.884	
BePxD12	48.2	100	Excluded	5.55	0.440	0.951	
PexD12	41.9	100	Excluded	5.40	0.382	0.932	
CORxD12	45	100	Excluded	6.39	0.411	0.993	

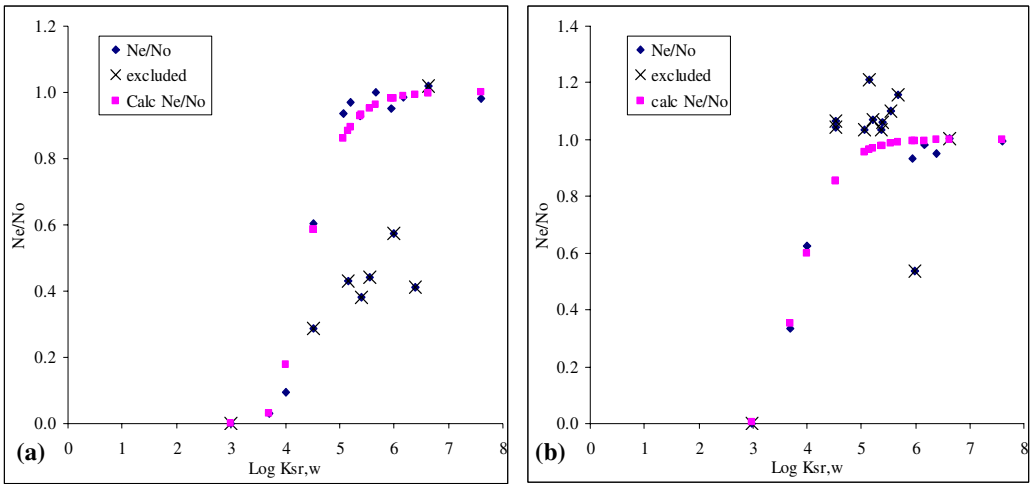

Figure 3.8: "S" shaped PRC dissipation curve for (a) Rinville Point, Galway Bay and (b) the NBL, Dublin Bay. The pink lines show the "best fit" curve (Excel Solver).

Example Calculations: *Measured and calculated Ne/No for PCB 10 in the Galway PS*

Equations presented in this example were obtained through personal communication with K. Yates [18] and F. Smedes [19].

The calculation involved in the determination of the "measured Ne/No" (Column "A" of *Table 3.6*) is shown here, using PCB 10 as a working example:

$$Ne/No = \frac{(\%PCB10 after\ exposure/(mean(\%PCB145 + \%PCB204 after\ exposure))}{(\%PCB10 before\ exposure/(mean(\%PCB145 + PCB204 before\ exposure))} \qquad \textbf{Eqn. 3.4}$$

Ne/No = (66.1/mean (111.5+107.6))/ (100/mean (100+100)) = 0.603

The Calculated Ne/No (Column "B" of *Table 3.6*) is determined based on a given R_S. Thus when the optimal R_S for Galway was derived, the value was calculated as follows:

Calc Ne/No= EXP(-R_S*Exposure time(d)/(sheet weight(g)/1000*10^$K_{sr,w}$ of PCB 10))

Calc Ne/No= EXP(-17.53*42/(20/1000*10^4.52)) = 0.584

The difference between the measured and calculated Ne/No are depicted in column "C" of *Table 3.6*. The difference for PCB 10 is thus calculated below:

Difference = (Ne/No) – (Calc Ne/No) = 0.603 - 0.584 = 0.0019

3.8.2.3 Conversion of PS Membrane Data into Water Concentration (C_w)

For estimation of the freely dissolved concentration (C_w) in the water phase the full uptake model valid for equilibrium and non-equilibrium situations is applied. The uptake is described by the following equation:

$$N^t = N^\infty \left(1 - e^{\frac{Rst}{MsKsr,w}}\right) \qquad \textbf{Eqn. 3.5}\ ^{(20)}$$

Where:

N^t is the amount of compound (ng) in the sampler after deployment for time t (days),

N^∞ is the final amount taken up in the equilibrium situation,

R_S the sampling rate (l/d),

t the exposure time (d),

Ms the mass of the sampler (kg),

$K_{sr,w}$ the silicone rubber-water partition co-efficient.

The final amount taken up in the equilibrium situation (N^{∞}) equals the equilibrium concentration (C_s^{∞}) times the mass of the sampler (Ms) in kg. C_s^{∞} is related to C_w by the partition coefficient $K_{sr,w}$ (l/kg) and consequently:

$$N^{\infty} = Ms * C_s^{\infty} = Ms * C_w * K_{sr,w} \quad \text{that gives} \quad C_w = \frac{N^{\infty}}{Ms * K_{sr,w}} \qquad \textbf{Eqn. 3.6}\ ^{(20)}$$

By combining *Eqn. 3.5* and *Eqn. 3.6*, the freely dissolved water concentrations (C_w) in ng/l were determined by means of the following equation:

$$C_w = \frac{N^t}{Ms * K_{sr,w}} * \frac{1}{1 - e^{\frac{R_s t}{Ms * K_{sr,w}}}} \qquad \textbf{Eqn. 3.7}\ ^{(20)}$$

In order to calculate C_w, silicone membrane specific partition constants ($K_{sr,w}$) are required. These $K_{sr,w}$ co-efficients were obtained in one of two ways;

- Utilisation of $K_{sr,w}$ available in the literature
- Estimated (modelled) using the available literature data.

Where $K_{sr,w}$ co-efficients were available in the literature [4] they were further used to generate the bi-plots presented in *Fig. 3.9*. The associated Log $K_{ow}/K_{sr,w}$ relationship was assumed to be linear for the hydrophobic compounds analysed in this study. Where only Log K_{ow} values were available for measured compounds the associated "modelled" $K_{sr,w}$ was estimated using the appropriate equation.

Literature and estimated $K_{sr,w}$ are presented in *Table 3.7* and were then utilised to derive dissolved water concentration for individual contaminants.

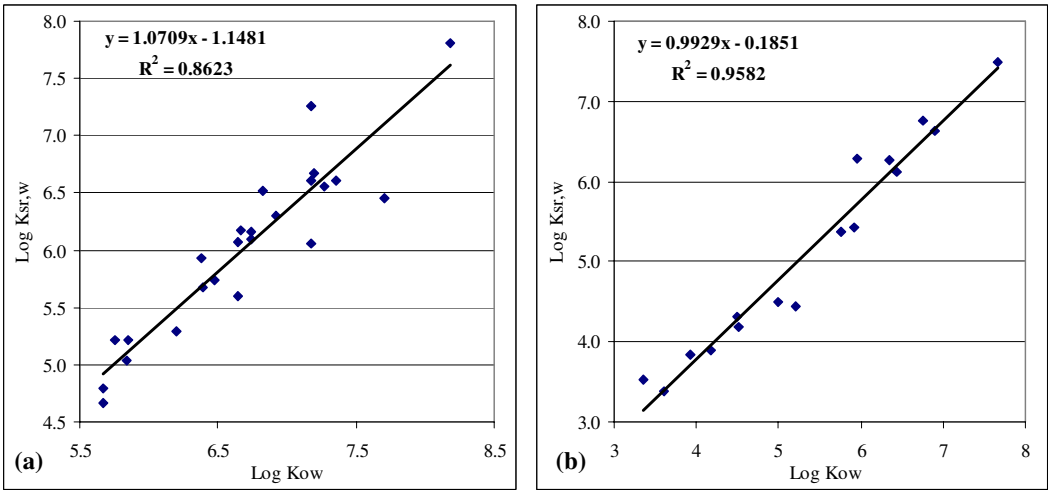

Figure 3.9: (a) PCB model and (b) PAH model generated for the estimation of missing $K_{sr,w}$ values.

The following equations were derived from the respective graphs by adding a trendline:

$$y = 1.0709x - 1.1481 \text{ (PCBs)} \qquad \textit{Eqn. 3.8}$$

$$y = 0.9929x - 0.1851 \text{ (PAHs)} \qquad \textit{Eqn. 3.9}$$

Worked example of calculating an estimated $K_{sr,w}$ for PCB18

PCB 18 was analysed as part of this assessment, however no literature Log $K_{sr,w}$ data are available for this compound, therefore a Log $K_{sr,w}$ was estimated using *Eqn. 3.8* as shown below.

$y = 1.0709x - 1.1481$
$y = 1.0709(\text{Log } K_{ow} \text{ of PCB 18}) - 1.1481$
$y = 1.0709(5.24) - 1.1481$
$y = 4.46$
Estimated Log $K_{sr,w} = 4.46$

Estimated Log $K_{sr,w}$ values have been completed for all compounds using *Eqn. 3.8* (PCBs) and *Eqn. 3.9* (PAHs) (See *Table 3.7*). This was completed irrespective of whether an actual literature Log $K_{sr,w}$ value was available in order to investigate the variance between literature and estimated values. PS derived water concentrations were then ultimately calculated for each compound of interest, using estimated and (where available) literature Log $K_{sr,w}$ values (*Table 4.13 - 4.15*).

Table 3.7: Octanol-water partition co-efficient values (Log K_{ow}) and estimated and literature (in parenthesis) [4] silicone rubber-water partition co-efficient values (Log $K_{sr,w}$) for the PCB and PAH compounds of interest in this study

Compound	Log K_{ow}	Log $K_{sr,w}$	Compound	Log K_{ow}	Log $K_{sr,w}$	Compound	Log K_{ow}	Log $K_{sr,w}$
PCB #18	5.24	4.46	PCB 126	6.89	6.23	PCB #206	8.09	7.52
PCB #28	5.67	4.92 (4.79)	PCB #128	6.74	6.07 (6.1)	PCB #208	7.71	7.11
PCB #31	5.67	4.92 (4.66)	PCB #129	6.73	6.06	PCB #209	8.18	7.61 (7.81)
PCB #33	5.6	4.85	PCB #138	6.83	6.17 (6.52)	Naphthalene	3.35	3.14 (3.53)
PCB #41	5.69	4.95	PCB #141	6.82	6.16	Acenaphthylene	3.61	3.40 (3.39)
PCB #44	5.75	5.01 (5.21)	PCB #149	6.67	5.99 (6.17)	Acenaphthene	3.92	3.71 (3.84)
PCB #47	5.85	5.12	PCB #151	6.64	5.96 (6.07)	Fluorene	4.18	3.97 (3.89)
PCB #49	5.85	5.12 (5.22)	PCB #153	6.92	6.26 (6.3)	Phenanthrene	4.52	4.30 (4.18)
PCB #51	5.63	4.88	PCB 156	7.18	6.54 (7.26)	Anthracene	4.50	4.28 (4.31)
PCB #52	5.84	5.11 (5.04)	PCB 157	7.18	6.54 (6.06)	Fluoranthene	5.20	4.98 (4.45)
PCB #56/#60	6.11	5.40	PCB 167	7.27	6.64	Pyrene	5.00	4.78 (4.49)
PCB #61	6.04	5.32	PCB 169	7.42	6.80	Benzo[b]naphtho[2,1-d]thiophene	5.34	5.12
PCB #66	6.2	5.49	PCB #170	7.27	6.64 (6.56)	Benzo[c]phenanthrene	5.76	5.53 (5.38)
PCB #74	6.2	5.49 (5.29)	PCB #180	7.36	6.73 (6.61)	Benzo[a]anthracene	5.91	5.68 (5.42)
PCB 77	6.36	5.66	PCB #183	7.2	6.56 (6.67)	Chrysene-Triphenylene	5.63	5.41
PCB 81	6.36	5.66	PCB #185	7.11	6.47	Benzo[ghi]fluoranthene	6.78	6.55
PCB #87	6.29	5.59	PCB #187	7.17	6.53 (6.61)	Benzo[b+k+j]fluoranthene	5.95	5.72 (6.29)
PCB #99	6.39	5.69 (5.68)	PCB 189	7.71	7.11 (6.45)	Benzo[e]pyrene	6.44	6.21 (6.12)
PCB #101	6.38	5.68 (5.93)	PCB #191	7.55	6.94	Benzo[a]pyrene	6.35	6.12 (6.27)
PCB 105	6.65	5.97 (5.6)	PCB #193	7.52	6.91	Indeno[1,2,3-cd]pyrene	7.66	7.42 (7.48)
PCB #110	6.48	5.79 (5.74)	PCB #194	7.8	7.20	Benzo[ghi]perylene	6.90	6.67 (6.63)
PCB 114	6.65	5.97	PCB #201	7.62	7.01	Anthanthrene	6.53	6.3
PCB 118	6.74	6.07 (6.16)	PCB #202	7.24	6.61	Dibenzo[ah]anthracene	6.75	6.52 (6.76)
PCB 123	6.74	6.07	PCB #203	7.65	7.04	Coronene	7.36	7.13

The Log K_{ow} values for PCBs were taken from Hawker and Connell [21] and the majority of those for PAHs from Sangster [22]. The Log $K_{sr,w}$ value for benzo[b+k+j]fluoranthene taken as an average of the values given by Yates et al [4] for benzo[b]fluoranthene and benzo[k]fluoranthene. The Log K_{ow} value for naphthacene was used for benzo[c]phenanthrene [4]. The Log K_{ow} values for benzo[a]anthracene, chrysene-triphenylene, benzo[ghi]fluoranthene and coronene were taken from www.env.gov.bc.ca/wat/wq/BCguidelines/pahs/pahs-01.htm [23], for benzo[b]naphtho[2,1-d]thiophene from Syracuse Research Corporation [24] and the Log K_{ow} for anthracene was taken from de Lima Ribeiro and Ferreira [25].

3.9 References

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CHAPTER 4: DISCUSSION OF RESULTS FROM THE PASSIVE SAMPLING TRIAL SURVEY (PSTS)

4.0 Introduction

The silicone rubber membranes, the mussels and the spot water samples were all analysed for PCBs and PAHs as described in Chapter Three. The results from the analysis are presented and discussed in this Chapter. For presentation and discussion purposes the results have been divided into the following related sections:

4.1 Physiological/biological characteristics of the mussels used in the study.

4.2 Cross validation exercise: Intercomparison studies

4.3 Evaluation of the Influence of using either Literature or Estimated Log $K_{sr,w}$ Values on MI PS derived PCB and PAH C_w

4.4 Introduction to the means of assessing test mussel tissue concentrations and the C_w as determined from the "spot" water samples and the silicone rubber PS

4.5 Assessment of PCB concentrations as determined in the various media

4.6 Assessment of PAH concentrations as determined in the various media

4.7 Investigation into the Generation of Mussel Models

The naming system applied to the mussel samples in this study are clarified herein. The mussels collected from the Rinville shoreline are known as the Galway T(start) mussels. A portion of these mussels was deployed at the Galway test site for 6 weeks in Galway Bay. The mussels retrieved with the PS device, post the exposure period, are referred to as the Galway T(end) mussels.

The Dublin mussels are named likewise, with the Dublin T(start) mussels representing those prior to the 6 week deployment and the Dublin T(end) mussels representing those retrieved after the exposure (T = 6 weeks). The native wild mussels collected from the Northbank Lighthouse are referred to as the Native NBL mussels. This native Dublin sample was taken on the day the PS device was retrieved from Dublin Bay (i.e. at T = 6

weeks). **Note:** The Dublin T(zero) mussels were originally transplanted from Galway to equilibrate at the NBL for 26 days prior to deployment with the Dublin PS device.

It is worth noting that during this Chapter, the PCB and PAH compounds are often referred to by their degree of chlorination (PCBs), their number of rings (PAHs) or molecular weight (PCBs and PAHs). *Table 4.1* clarifies the number of chlorine atoms present in each PCB compound, with members of the mono-penta groups (1-5 Cl atoms, PCB 1-127) referred to as the less chlorinated and the hexa-deca groups (6-10 Cl atoms, PCB 128-209) referred to as the heavier chlorinated compounds. As regards the PAHs, those with 3 benzene rings are classed as the lower molecular weight PAHs, while those with 4+ rings are known as the higher molecular weight compounds (*Table 4.2*).

Table 4.1: Degree of chlorination and molecular weights of PCBs [1, 2]

PCB range	PCB Group	No of Cl atoms	Formula	Molecular Weight
1-3	Monochlorobiphenyls	1	$C_{12}H_9Cl_1$	189.0
4-15	Dichlorobiphenyls	2	$C_{12}H_8Cl_2$	233.1
16-39	Trichlorobiphenyls	3	$C_{12}H_7Cl_3$	257.5
40-81	Tetrachlorobiphenyls	4	$C_{12}H_6Cl_4$	292
82-127	Pentachlorobiphenyls	5	$C_{12}H_5Cl_5$	326
128-169	Hexachlorobiphenyls	6	$C_{12}H_4Cl_6$	361
170-193	Heptachlorobiphenyls	7	$C_{12}H_3Cl_7$	395.3
194-205	Octachlorobiphenyls	8	$C_{12}H_2Cl_8$	430.0
206-208	Nonachlorobiphenyls	9	$C_{12}H_1Cl_9$	464.2
209	Decachlorobiphenyls	10	$C_{12}Cl_{10}$	498.6

Table 4.2: Ring structures and molecular weights of PAHs [3-7]

PAH (Symbol)	Molecular Weight	Rings
Naphthalene (N)	128.2	2A
Acenaphthylene (Acy)	152.2	2A1C
Acenaphthene (Ace)	154.2	2A1C
Fluorene (F)	166.2	2A1C
Phenanthrene (P)	178.2	3A
Anthracene (A)	178.2	3A
Fluoranthene (Fl)	202.3	3A1C
Pyrene (Py)	202.3	4A
Benzo[ghi]fluoranthene (BghiF)	214.2	4A1C
Benzo[a]anthracene (BaA)	228.3	4A
Chrysene (C)	228.3	4A
Benzo[c]phenanthrene (BcP)	228.29	4A
Benzo[b]naphtho[2,1-d]thiophene (BbN)	234.32	3A1C
Benzo[b]fluoranthene (BbF)	252.3	4A1C
Benzo[k]fluoranthene (BkF)	252.3	4A1C
Benzo[a]pyrene (BaP)	252.3	5A
Benzo[e]pyrene (BeP)	252	5A
Indeno[1,2,3,-cd]pyrene (IP)	276.0	5A1C
Benzo[ghi]perylene (BghiP)	276.3	5A1C
Anthanthrene (An)	276.34	6A
Dibenzo[ah]anthracene (DahA)	278.4	5A
Coronene (Co)	300.3	7A

A: aromatic; C: nonaromatic

4.1 Physiological/Biological Characteristics of the Study Mussels

Study mussels (n=50 to 60 individuals) were sourced from Galway Bay and were size classed (40-60mm) prior to the start of the study in order to minimise the potential for size related differences in uptake/metabolism within the mussels. A native blue mussel sample was additionally collected at the Dublin Bay (NBL) site at the end of the exposure study period for comparison purposes.

Mean shell lengths (and Standard deviation) were similar for all test site samples and ranged from (51.2 to 55.5 mm with 2.17 to 3.51 mm stdev) over the duration of the study. The overall condition (as measured by the proxy condition index as per Section 3.6.1, See *Table 4.3*) of study mussels is discussed below.

The condition of the Dublin transplanted mussels at the end of the exposure study [C.I.=10] was slightly lower than their Galway counterparts [C.I.=13], possibly indicating that the mussels found it difficult to adjust to conditions in Dublin Bay compared to their original site. Native Dublin Bay mussels exhibited a greater overall condition index [C.I.=16] compared to other mussels tested, by having the combination of the greatest amount of flesh per mussel (0.8 g dry weight) and the smallest mean shell length (51.2 mm).

According to Hellou et al [(8)], combined toxic effects due to multiple stressors would be expected to lead to reduced growth in *Mytilus edulis* while chemical stress would be linked to increased lipids. From the data in *Table 4.3*, the Native NBL mussels display both the highest lipid content and condition index. The wellbeing of these mussels would be expected to integrate exposure conditions over the long-term and to be due to a combination of variables such as currents, variety and quality of food.

Mussels with a higher lipid content have been documented to bioaccumulate higher levels of lipophilic contaminants [9, 10], while at the same time, continuous exposure to contaminants has been observed to increase lipid content [11, 12]. Whether the Native NBL mussels contain the highest level of contaminants (*Table 4.16* (PCB) and *Table 4.17* (PAH)) as a result of their high lipid content, or have the highest lipid content as a result of the continuous exposure to contaminants remains unclear.

Results for total lipid content as measured using the Smedes method (Appendix 2) were comparable to the extractable lipid, indicating that the extraction procedure used for contaminant analysis was exhaustive (See *Table 4.3*).

Table 4.3: Physiological parameters of mussel samples throughout the study and site specific environmental parameters taken at the start of the deployment study

Sample Location	**Galway**		**Dublin**		
	T(start)	**T(end)**	**T(start)**	**T(end)**	**Native NBL**
Sample size (Number of mussels)	50	60	50	60	60
Mean shell length (mm)	55.5	55	55.2	54.6	51.2
Standard deviation (mm)	2.17	2.27	2.54	2.91	3.51
Total flesh (g wet wgt)	167	229	145	167	219
Average dry weight (%)	19.8	18.4	20.1	20	22
Total flesh (g dry wgt)	33.2	42.2	29.2	33.4	48.2
Flesh/mussel (g dry wgt)	0.66	0.70	0.58	0.56	0.80
C.I. (dry wgt/shell length)	12	13	11	10	16
% extractable lipid* (total lipid)	1.30 (1.30)	1.40 (1.37)	1.20 (1.27)	1.21 (1.25)	2.02 (1.93)
Water temperature (^{o}C)	8.65		8.26		
Air temperature (^{o}C)	4.6		7.3		
Salinity (PSU)	22.6		26.8		
Suspended solids (mg/l)	5		20.6		
Dissolved oxygen (%)(mg/l)	100 (10.1)		101 (9.98)		
pH (pH units)	7.99		8.01		

C.I= Condition Index, based on the division of the average dry weight of tissue by the average shell length and the resulting answer is then multiplied by 1000. *Percentage extractable lipid in each pooled mussel sample. These values were used to convert pollutant concentrations from a lipid weight to wet and dry weight basis. Value in parenthesis, total lipid as determined in the same samples by the Smedes lipid extraction method. This second determination is for comparison purposes only and is not used elsewhere.

4.2 Cross Validation of Methodology: Inter-comparison Exercise

Cross validation of the PS methodology was completed through the analysis of duplicate PS membranes by two separate laboratories. In order to carry out an inter-laboratory comparison, the PCB and PAH levels detected in the membranes and the subsequent derived water concentrations as determined by both the MI and the Reference Laboratory are discussed herein. This assessment is broken into two components, namely;

4.2.1 Assessment of membrane PCB and PAH results from the MI and Reference laboratory.

4.2.2 Assessment of MI and Reference laboratory PS derived water concentrations for PCBs and PAHs.

Comparison of the results obtained by both parties on representative aliquots of the passive sampling membranes provides an indication of the robustness of analytical methodologies completed by both laboratories.

4.2.1 Assessment of Membrane PCB and PAH Results from the MI and Reference Laboratory

The contaminant concentrations determined by the MI and the Reference laboratory, and the percentage difference between the data sets, are presented in *Table 4.4* and *Table 4.5*. In both instances analytical data are reported "normalised" to 20g membrane weight equivalents.

4.2.1.1 Assessment of Membrane PCB Results

Table 4.4 presents the list of compounds analysed in the duplicate PS membranes by both the MI and the Reference laboratory. Graphical representations have been expressed as Log(x+1) in the Figures below.

Table 4.4: Percentage difference between the PCB concentrations (ng/20g PS membrane) provided by the Marine Institute (MI) and the Reference laboratory (Ref)

Sample	Galway			Dublin			Blank
Laboratory	MI	Ref	% diff	MI	Ref	% diff	MI
CB18	0.99	1.10	-10.0	3.05	3.35	-8.96	<0.71
CB28	2.03	2.50	-18.8	4.09	4.54	-9.91	<0.82
CB31	6.07	0.83	631	8.05	2.18	269	5.29
CB44	0.63	2.58	-75.6	2.02	2.57	-21.4	<0.24
CB52	1.95	2.41	-19.1	4.66	3.96	17.7	0.54
CB101	1.23	0.87	41.4	2.84	2.43	16.9	<0.47
CB118	0.48	2.77	-82.7	1.30	1.62	-19.8	<0.22
CB138	0.66	0.57	15.8	1.12	1.45	-22.8	<0.59
CB153	0.68	0.94	-27.7	0.79	1.55	-49.0	<0.47
CB170	<0.13	0.12		<0.12	0.13		<0.24
CB180	0.14	0.15	-6.7	0.18	0.32	-43.8	<0.24
CB187	0.48	0.34	41.2	0.40	0.41	-2.44	0.30

Overall the Dublin PCB concentrations, as determined by both parties, are generally higher than those in Galway (*Table 4.4*, *Fig. 4.1*). There are few exceptions i.e. the concentration of PCB 187 detected by the MI and the concentrations of PCB 44 and PCB 118 detected by the Reference laboratory are greater in the Galway PS.

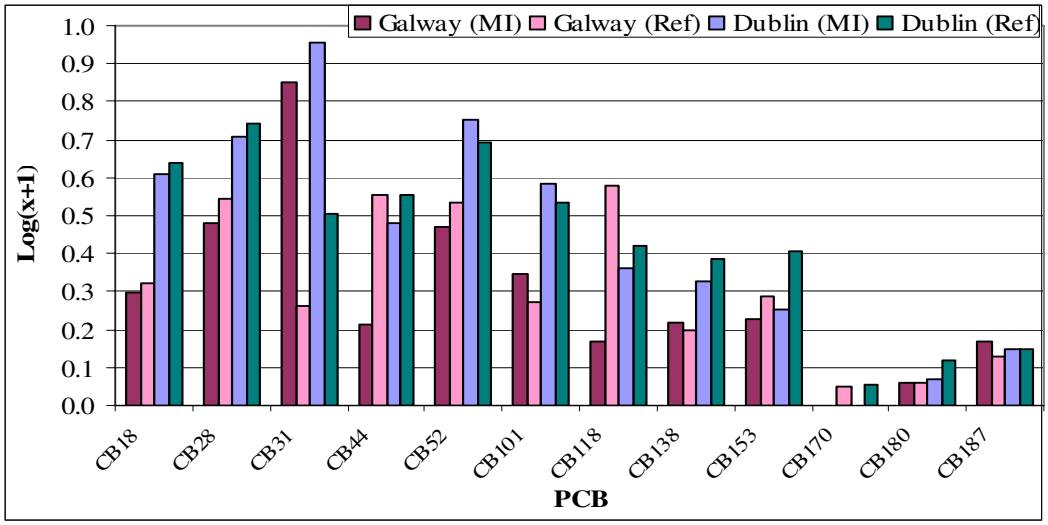

Figure 4.1: PCB concentrations (ng/20g PS membrane) as provided by the Marine Institute (MI) and the Reference laboratory (Ref).

In general higher concentrations of PCBs 18, 28, 44, 118, 153 and 180 were detected in the PS membranes analysed by the Reference Laboratory, while the MI detected higher concentrations of PCB 31 and PCB 101. It should be noted that elevated blank concentrations were also reported by the MI for PCB 31 (*Table 4.4*). PCB 170 was not detected by the MI in either the Galway or Dublin membranes. The concentration of PCB 52 was higher in the Galway PS analysed by the Reference laboratory than that analysed by the MI, with the reverse being true for the Dublin PS membranes. Concentrations of PCB 138 and PCB 187 were higher in the Galway PS analysed by the MI than that analysed by the Reference laboratory, again with the reverse being true for the Dublin PS membranes.

The greatest percentage difference observed between the data obtained from the MI and Reference Laboratory was for PCB 31, whereby the MI value was 631 % (Galway) and 269 % (Dublin) higher than that reported by the Reference laboratory for duplicate membranes. Co-elution of compounds may have occurred during the analysis of the membranes by the MI, which would account for such a high percentage difference.

The remaining percentage differences reported for the Galway PS indicate that the MI results range from being 75.6 % less than to 41.2 % greater than the equivalent Reference laboratory figures. The range is closer in the Dublin PS, with the MI results ranging from a difference of 49 % less than to 17.7 % greater than the corresponding Reference laboratory results.

4.2.1.2 Assessment of Membrane PAH Results

PAHs were also analysed by both the Reference laboratory and the MI. As per the PCBs (*Fig. 4.1*), graphical representation of the PAH data has been expressed as Log(x+1) in

Fig. 4.2 below. With the exception of naphthalene, PAH concentrations determined from the Dublin PS membranes, by both parties, are higher than those in the Galway PS (See *Table 4.5* and *Fig. 4.2*).

Table 4.5: Percentage difference between the PAH concentrations (ng/20g PS membrane) provided by the Marine Institute (MI) and the Reference laboratory (Ref)

Sample	Galway			Dublin			Blank
Laboratory	MI	Ref	% diff	MI	Ref	% diff	MI
Naphthalene (N)	790	663	19.2	341	322	5.90	113
Acenaphthylene (Acy)	46.3	39.6	16.9	142	113	25.7	<16.8
Acenaphthene (Ace)	45.6	69.5	-34.4	112	292	-61.6	11.3
Fluorene (F)	302	200	51.0	689	554	24.4	27.4
Phenanthrene (P)	1,258	1,147	9.68	1,694	1,660	2.05	60.3
Anthracene (A)	95.8	94.3	1.59	136	215	-36.7	3.00
Fluoranthene (Fl)	1,027	747	37.5	1,263	967	30.6	34.7
Pyrene (Py)	796	606	31.4	1,461	1,162	25.7	26.3
Benzo[a]anthracene (BaA)	85.9	52.0	65.2	162	107	51.4	3.55
Chrysene-Triphenylene (C-T) *	359	69.4		444	127		14.4
Benzo[a]pyrene (BaP)	25.1	7.40	239	40.1	24.7	62.3	12.9
Indeno[1,2,3-cd]pyrene (IP)	5.23	2.88	81.6	9.74	7.21	35.1	<5.59
Benzo[ghi]perylene (BghiP)	9.87	3.55	178	14.3	9.64	48.3	<3.92
Benzo[e]pyrene (BeP)	28.8	22.7	26.9	54.7	63.7	-14.1	<2.24

* Chrysene was reported individually by the Reference laboratory and as a combination of Chrysene-Triphenylene (co-elution) by the MI.

Concentrations of acenaphthene in Galway, and acenaphthene, anthracene and benzo[e]pyrene in Dublin are more elevated for the reference laboratory than for the MI, with the reverse being true for the remaining compounds.

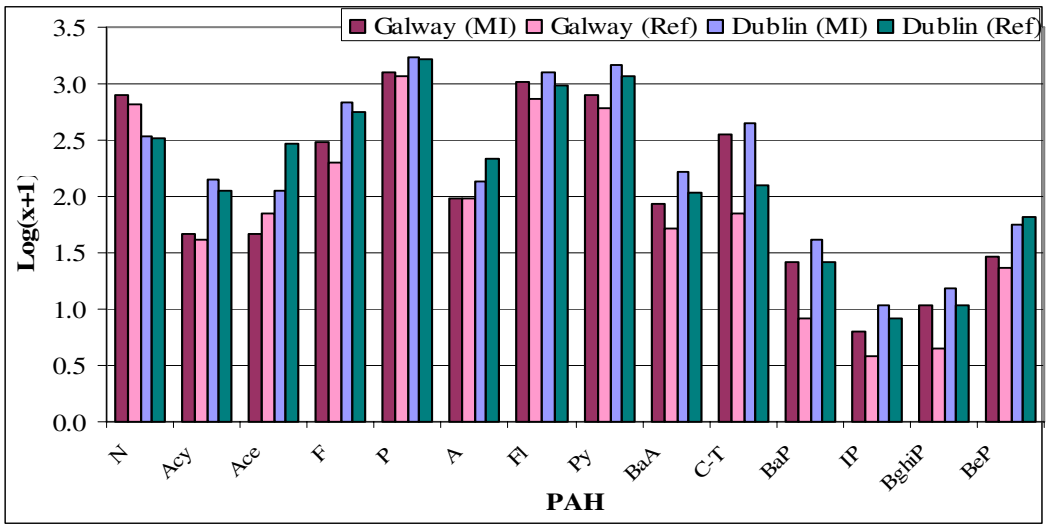

Figure 4.2: PAH concentrations (ng/20 PS membrane) as provided by the Marine Institute (MI) and the Reference laboratory (Ref).

The greatest percentage differences observed between the data obtained from the MI and Reference Laboratory was for benzo[a]pyrene, whereby the MI values were 239 % (Galway) and 62.3 % (Dublin) higher than those reported by the Reference laboratory for duplicate membranes. The benzo[ghi]perylene concentration in the Galway membranes also had a considerable percentage difference, with the MI value being 178% greater than the Reference laboratory value. As was the possible cause for high percentage differences experienced for PCB 31, co-elution of compounds during the analysis of membranes by the MI may account for the high percentage differences experienced for benzo[a]pyrene and benzo[ghi]perylene.

The remaining percentage differences reported for the Galway PS indicate that the MI results range from being 34.4 % less than to 81.6 % greater than the equivalent Reference laboratory figures, while the Dublin PS range is similar, with the MI results ranging from a difference of 61.6 % less than to 51.4 % greater than the corresponding Reference laboratory results.

While results suggest a disparity in concentrations, it should be noted that these results have not yet been corrected for PRCs. Thus, assuming that the analyses of PRCs behave in a similar manner, it would be expected that this percentage of disparity would decrease. Differences between MI and Reference laboratory concentrations when corrected for PRCs are further discussed in Section 4.2.2 below.

4.2.2. Assessment of MI and Reference Laboratory PS derived C_w

Following on from 4.2.1 above, water concentrations of the various contaminants were derived from the passive sampling membranes. As previously discussed, a number of differences in membrane concentrations were evident as a result of separate laboratory

analysis (MI and Reference Laboratory). As passive sampling membrane concentrations differ and when coupled with differences in sampling rates (R_S) (as determined from both sets of analytical data), it would be expected that derived dissolved water concentrations (C_w) would also show a range of values.

It is worth noting that the literature Log $K_{sr,w}$ values for PCB and PAH compounds used up to this point were those taken from work carried out by Yates et al [13]. Also, the estimated Log $K_{sr,w}$ values determined in Section 3.8.2.3 were modelled from those same literature values. However, in this Section another set of Log $K_{sr,w}$ values are introduced by Smedes [14]. This second set of Log $K_{sr,w}$ values are referred to as the Smedes values from here onwards (See *Table 4.6*).

Table 4.6: Log $K_{sr,w}$ values available for a limited range of PCB and PAH compounds from both Yates et al [13] and Smedes [14]

Compound	Log $K_{sr,w}$ values		Compound	Log $K_{sr,w}$ values	
	Smedes	Yates		Smedes	Yates
CB18	5.18	4.46	**Acenaphthylene**	3.21	3.39
CB28	5.46	4.79	**Acenaphthene**	3.57	3.84
CB31	5.43	4.66	**Fluorene**	3.74	3.89
CB44	5.76	5.21	**Phenanthrene**	4.05	4.18
CB52	5.75	5.04	**Anthracene**	4.15	4.31
CB101	6.22	5.93	**Fluoranthene**	4.57	4.45
CB118	6.35	6.16	**Pyrene**	4.63	4.49
CB138	6.68	6.52	**Benzo[a]anthracene**	5.25	5.42
CB153	6.66	6.30	**Chrysene-Triphenylene**	5.19	5.41
CB170	7.07	6.56	**Benzo[e]pyrene**	5.59	6.12
CB180	6.93	6.61	**Benzo[a]pyrene**	5.66	6.27
CB187	6.76	6.61	**Benzo[ghi]perylene**	6.00	6.63
Naphthalene	2.98	3.53	**Indeno[1,2,3-cd]pyrene**	6.07	7.48

As the Smedes [14] set of contaminant Log $K_{sr,w}$ values are not as extensive as those provided by Yates et al [13] (*Table 3.7*), they are used only in this Section for comparative purposes and are not used elsewhere throughout the thesis. As regards the Log $K_{sr,w}$ values for the PRC compounds (used in the determination of the site specific R_S), they were provided by Smedes [14] as Yates et al [13] had no such values available.

In order to further evaluate the extent of such differences (and further validate the robustness of the technique), the PS membrane analytical data (*Table 4.4* and *Table 4.5*) and sampling rates (Dublin: 2.38 l/d (MI); 4.93 l/d (Ref) and Galway 8.48 l/d (MI); 10.2 l/d (Ref)) determined by the MI and Reference laboratory were used to derive dissolved C_w of contaminants for both Galway and Dublin using both sets of Log $K_{sr,w}$ values.

Table 4.7 and *Table 4.8* present the PS derived water concentration data for the PCB and PAH compounds as analysed in duplicate PS membranes from Galway and Dublin by both the MI and the Reference laboratory. A total of 12 PCBs (7 marker PCBs (PCB 118 being also a WHO PCB), in addition to 5 "other" PCBs) and 14 PAHs were tested by both parties. This Section deals with:

4.2.3 The PCB and PAH C_w determined by the MI and Reference laboratory, using different Log $K_{sr,w}$ values (Yates et al [13] and Smedes [14]).

4.2.4 An inter-laboratory comparison of PCB and PAH water concentrations, whereby concentrations were determined from both laboratories using the same Log $K_{sr,w}$ values.

4.2.5 The effect of altering the sampling rate (R_S)

4.2.3 PCB and PAH C_w determined by the MI and the Reference Laboratory, using Different Log $K_{sr,w}$ Values.

The MI and Reference laboratories used their own membrane contaminant concentration data and PRC derived R_S values to determine the PS derived PCB and PAH C_w water concentrations shown in *Table 4.7* (PCB) and *Table 4.8* (PAH). However, as regards the Log $K_{sr,w}$ values used, the PS derived C_w in the MI and Ref columns of the tables below were determined using Log $K_{sr,w}$ values from Yates et al [13] and Smedes [14] (in parenthesis).

Table 4.7: Percentage difference between PS derived PCB C_w (pg/l) as determined using Log $K_{sr,w}$ values from Yates et al [13] and (in parenthesis), Smedes [14] (See *Table 4.6*) by both the Marine Institute (MI) and the Reference laboratory (Ref). Analysis was carried out of duplicate membrane samples taken from the Galway the Dublin sites

Location	Galway				Dublin			
Laboratory	MI		Reference		MI		Reference	
	C_w	% diff	C_w	% diff	C_w	% diff	C_w	% diff
CB18	3.73 (2.95)	26.4	3.63 (2.75)	32.1	31.9 (29.7)	7.48	18.5 (16.0)	15.8
CB28	6.56 (5.87)	11.7	6.90 (6.05)	14.1	40.7 (39.4)	3.36	22.8 (21.3)	7.03
CB31	20.6 (17.6)	16.8	2.43 (2.01)	20.4	81.4 (77.6)	4.81	11.3 (10.3)	10.1
CB44	1.86 (1.79)	3.97	6.43 (6.13)	4.79	19.6 (19.4)	1.16	12.3 (12.0)	2.41
CB52	5.94 (5.57)	6.64	6.20 (5.74)	8.02	45.6 (44.7)	1.93	19.2 (18.4)	4.02
CB101	3.48 (3.46)	0.51	2.06 (2.05)	0.61	27.2 (27.2)	0.15	11.3 (11.2)	0.31
CB118	1.35 (1.35)	0.22	6.52 (6.51)	0.26	12.4 (12.4)	0.06	7.51 (7.50)	0.13
CB138	1.85 (1.84)	0.08	1.35 (1.34)	0.10	10.7 (10.7)	0.02	6.68 (6.68)	0.05
CB153	1.93 (1.92)	0.25	2.20 (2.19)	0.30	7.58 (7.58)	0.07	7.17 (7.16)	0.15
CB170	< 0.36 (< 0.36)	0.17	0.28 (0.28)	0.20	< 1.12 (< 1.12)	0.05	0.59 (0.59)	0.10
CB180	0.40 (0.40)	0.11	0.35 (0.35)	0.14	1.70 (1.70)	0.03	1.46 (1.46)	0.07
CB187	1.35 (1.35)	0.06	0.80 (0.80)	0.08	3.83 (3.82)	0.02	1.90 (1.90)	0.04

The Log $K_{sr,w}$ value for CB 18 (not in parenthesis) is an estimated value (See Section 3.8.2.3).

Table 4.8: Percentage difference between PS derived PAH C_w (pg/l) as determined using Log $K_{sr,w}$ values from Yates et al [13] and (in parenthesis), Smedes [14] (See *Table 4.6*) by both the Marine Institute (MI) and the Reference laboratory (Ref). Analysis was carried out of duplicate membrane samples taken from the Galway the Dublin sites

Location	Galway				Dublin			
Laboratory	MI		Reference		MI		Reference	
	C_w	% diff	C_w	% diff	C_w	% diff	C_w	% diff
N	11,721 (41,372)	-71.7	9,807 (34,733)	-71.8	6,392 (17,917)	-64.3	4,948 (16,843)	-70.6
Acy	930 (1,407)	-33.9	807 (1,222)	-33.9	2,594 (3,603)	-28.0	2,328 (3,486)	-33.2
Ace	362 (628)	-42.3	526 (938)	-43.9	1,937 (2,534)	-23.6	2,663 (4,149)	-35.8
F	2,162 (2,857)	-24.3	1,373 (1,854)	-26.0	9,041 (10,199)	-11.4	4,740 (5,853)	-19.0
P	6,010 (7,049)	-14.7	5,006 (6,002)	-16.6	19,133 (20,241)	-5.47	10,719 (11,938)	-10.2
A	403 (473)	-14.8	355 (428)	-16.9	1,473 (1,555)	-5.27	1,277 (1,419)	-10.0
Fl	3,889 (3,629)	7.17	2,490 (2,295)	8.50	13,211 (12,925)	2.21	5,372 (5,142)	4.48
Py	2,940 (2,733)	7.56	1,962 (1,800)	8.99	15,170 (14,828)	2.30	6,352 (6,067)	4.70
BaA	250 (254)	-1.59	126 (129)	-1.90	1,564 (1,571)	-0.47	503 (507)	-0.97
C-T	1,045 (1,068)	-2.21	169 (173)	-2.65	4,285 (4,314)	-0.66	599 (607)	-1.36
BeP	81.4 (82.7)	-1.59	53.3 (54.4)	-1.91	523 (526)	-0.47	295 (298)	-0.97
BaP	70.8 (71.9)	-1.45	17.4 (17.7)	-1.74	383 (385)	-0.43	114 (115)	-0.89
BghiP	27.8 (28.0)	-0.68	8.31 (8.38)	-0.81	137 (137)	-0.20	44.5 (44.7)	-0.41
IP	14.7 (14.8)	-0.72	6.72 (6.78)	-0.87	93.0 (93.2)	-0.21	33.2 (33.4)	-0.44

The Log $K_{sr,w}$ value for chrysene-triphenylene (not in parenthesis) is an estimated value (See Section 3.8.2.3).

Equivalent dissolved PCB C_w as determined using the Log $K_{sr,w}$ values from Yates et al [13] are consistently higher than those determined using Log $K_{sr,w}$ values from Smedes [14] (in parenthesis) (*Table 4.7*). From *Table 4.8*, it appears that the equivalent dissolved PAH C_w as determined using the Log $K_{sr,w}$ values from Yates et al [13] are generally lower (exception fluoranthene and pyrene) than those determined using Log $K_{sr,w}$ values from Smedes [14] (in parenthesis), while the reverse is true for fluoranthene and pyrene concentrations (those determined using Yates et al [13] values are higher than those determined using Smedes'[14]) (See *Table 4.6* for Log $K_{sr,w}$ values).

On comparing the PS derived PCB and PAH C_w (*Table 4.7* and *Table 4.8*) with the Log $K_{sr,w}$ values used to determine them (*Table 4.6*), a similar trend arises for both contaminant groups. The lower the Log $K_{sr,w}$ value used to determine the equivalent PS derived water concentration, the greater the resultant concentration (and vice versa) e.g. when the Log $K_{sr,w}$ value for anthracene decreased from 4.31 (Yates et al) to 4.15 (Smedes) with all other parameters in the equation remaining unchanged (*Eqn. 3.7*), the anthracene concentration determined by the MI from the Galway membrane increased from 403 pg/l (Yates et al) to 473 pg/l (Smedes).

As regards the percentage difference in contaminant C_w determined for each laboratory, using Log $K_{sr,w}$ values from either Yates et al [13] or Smedes [14], it appears that the percentage difference increases with decreasing molecular weight. Since a decrease in molecular weight relates directly to a decrease in Log $K_{sr,w}$ value, the impact of varying the Log $K_{sr,w}$ value on the determination of the C_w therefore becomes more evident.

The PCB C_w (*Table 4.7*) determined using Log $K_{sr,w}$ values from Yates et al [13] for the more chlorinated PCBs (i.e. PCB 101 upwards), are no more than 0.61 % greater than those determined using the Log $K_{sr,w}$ values from Smedes [14]. The percentage differences are greater in the case of the lower chlorinated PCBs, ranging from 1.16 % to 32.1 %. The C_w of the less chlorinated PCBs arranged in order of decreasing percentage differences from *Table 4.7* above are as follows: PCB 18>31>28>52>44.

While the PCB data in *Table 4.7* above indicates that slight difference in Log $K_{sr,w}$ value (*Table 4.6*) would not heavily influence the final PS derived C_w i.e. when different Log $K_{sr,w}$ values were used to derive PCB C_w from the same laboratory's data set, the

percentage differences were relatively low (majority below 0.61 %, with a maximum difference of 32.1 %), the PAH data in *Table 4.8* above suggests otherwise.

The majority of PAH compounds have acceptable percentage differences (*Table 4.8*), however those compounds with only two benzene rings have percentage differences ranging from 19 % to 71.1 %. The C_w of such PAHs arranged in order of decreasing percentage differences are as follows: naphthalene > acenaphthene > acenaphthylene > fluorene, with acenaphthene and acenaphthylene in reverse positions for Dublin MI sample.

From the PAH data in *Table 4.8*, it becomes more apparent that the percentage difference increases as Log $K_{sr,w}$ values decrease (molecular weight decreases). This is shown though the following example taken from *Table 4.8*: Two PAH compounds which have approximately the same difference in Log $K_{sr,w}$ values (~ 0.5) i.e. Log $K_{sr,w}$ values for naphthalene are 3.53 (Yates et al); 2.98 (Smedes) and for benzo[e]pyrene are 6.12 (Yates et al); 5.59 (Smedes). While a similar drop of ~ 0.5 in Log $K_{sr,w}$ value causes a decrease in final water concentration of 71.1 % in the naphthalene (low molecular weight/low Log $K_{sr,w}$ compound), it results in a mere decrease of 1.59 % in the concentration of benzo[e]pyrene (higher molecular weight/higher Log $K_{sr,w}$ compound) (See the Galway MI column of *Table 4.8*).

In order to ensure the differences seen above are not related to the membrane concentration data, the following investigation was completed. The concentration of naphthalene determined by the MI for the Galway PS was 790 ng/20g membrane. This value was entered into *Eqn. 3.7* to derive the equivalent dissolved water concentration. All parameters remaining constant in this equation, except for the Log $K_{sr,w}$ values (3.53

(Yates et al); 2.98 (Smedes)), resulted in a percentage difference of 71.1 % between the derived water concentrations. In order to prove that the membrane concentration does not unduly influence the percentage difference observed, the calculation was repeated using a concentration of 7.90 ng/20g membrane. Again the two different Log $K_{sr,w}$ values were used, and although the resulting PS derived water concentrations were much lower, the same percentage difference was observed.

4.2.4 Inter-Laboratory Comparison of PCB and PAH C_w determined using the Same Log $K_{sr,w}$ Values

The percentage differences illustrated in *Table 4.9* (PCB) and *Table 4.10* (PAH) refer to the percentage differences between the dissolved water concentrations as determined by the MI and Reference laboratory when both parties use the same Log $K_{sr,w}$ values (first using Yates et al [13] values and then Smedes [14]) (See *Table 4.9* and *Table 4.10*).

Table 4.9: PS derived PCB C_w (pg/l) as determined from duplicate membrane samples taken from Galway and Dublin, and subsequently analysed by the Marine Institute (MI) and the Reference laboratory (Ref). Percentage differences in the water concentrations as determined by each laboratory using Log $K_{sr,w}$ values from Yates et al [13] and Smedes [14] are shown

Location	**Galway**				**Dublin**			
Laboratory	**Yates**		**Smedes**		**Yates**		**Smedes**	
	MI (Ref)	**% diff**	**MI (Ref)**	**% diff**	**MI (Ref)**	**% diff**	**MI (Ref)**	**% diff**
CB18	3.73 (3.63)	2.76	2.95 (2.75)	7.37	31.9 (18.5)	72.1	29.7 (16.0)	85.4
CB28	6.56 (6.90)	-4.97	5.87 (6.05)	-2.90	40.7 (22.8)	78.6	39.4 (21.3)	84.9
CB31	20.6 (2.43)	749	17.6 (2.01)	775	81.4 (11.3)	621	77.6 (10.3)	657
CB44	1.86 (6.43)	-71.0	1.79 (6.13)	-70.8	19.6 (12.3)	60.2	19.4 (12.0)	62.1
CB52	5.94 (6.20)	-4.24	5.57 (5.74)	-3.01	45.6 (19.2)	138	44.7 (18.4)	143
CB101	3.48 (2.06)	68.9	3.46 (2.05)	69.1	27.2 (11.3)	142	27.2 (11.2)	142
CB118	1.35 (6.52)	-79.3	1.35 (6.51)	-79.2	12.4 (7.51)	65.7	12.4 (7.50)	65.8
CB138	1.85 (1.35)	37.1	1.84 (1.34)	37.1	10.7 (6.68)	60.1	10.7 (6.68)	60.2
CB153	1.93 (2.20)	-12.3	1.92 (2.19)	-12.2	7.58 (7.17)	5.76	7.58 (7.16)	5.85
CB170	< 0.36 (0.28)	28.5	< 0.36 (0.28)	28.6	1.12 (0.59)	90.0	1.12 (0.59)	90.1
CB180	0.40 (0.35)	15.3	0.40 (0.35)	15.4	1.70 (1.46)	16.5	1.70 (1.46)	16.5
CB187	1.35 (0.80)	67.6	1.35 (0.80)	67.6	3.83 (1.90)	101	3.82 (1.90)	101

The PS derived C_w for Galway and Dublin were determined by the MI and (in parenthesis), the Reference laboratory.

Table 4.10: PS derived PAH C_w (pg/l) as determined from duplicate membrane samples taken from Galway and Dublin, and subsequently analysed by the Marine Institute (MI) and the Reference laboratory (Ref). Percentage differences in the water concentrations as determined by each laboratory using Log $K_{sr,w}$ values from Yates et al [13] and Smedes [14] are shown

Location	Galway				Dublin			
Laboratory	Yates		Smedes		Yates		Smedes	
	MI (Ref)	% diff	MI (Ref)	% diff	MI (Ref)	% diff	MI (Ref)	% diff
N	11,721 (9,807)	19.5	41,372 (34,733)	19.1	6,392 (4,948)	29.2	17,917 (16,843)	6.38
Acy	930 (807)	15.2	1,407 (1,222)	15.2	2,594 (2,328)	11.4	3,603 (3,486)	3.37
Ace	362 (526)	-31.1	628 (938)	-33.0	1,937 (2,663)	-27.3	2,534 (4,149)	-38.9
F	2,162 (1,373)	57.4	2,857 (1,854)	54.1	9,041 (4,740)	90.8	10,199 (5,853)	74.3
P	6,010 (5,006)	20.1	7,049 (6,002)	17.5	19,133 (10,719)	78.5	20,241 (11,938)	69.5
A	403 (355)	13.5	473 (428)	10.8	1,473 (1,277)	15.4	1,555 (1,419)	9.6
Fl	3,889 (2,490)	56.2	3,629 (2,295)	58.1	13,211 (5,372)	146	12,925 (5,142)	151
Py	2,940 (1,962)	49.9	2,733 (1,800)	51.9	15,170 (6,352)	139	14,828 (6,067)	144
BaA	250 (126)	97.4	254 (129)	96.8	1,564 (503)	211	1,571 (507)	210
C-T	1,045 (169)	519	1,068 (173)	516	4,285 (599)	616	4,314 (607)	611
BeP	81.4 (53.3)	52.6	82.7 (54.4)	52.1	523 (295)	77.4	526 (298)	76.5
BaP	70.8 (17.4)	307	71.9 (17.7)	306	383 (114)	235	385 (115)	234
BghiP	27.8 (8.31)	234	28.0 (8.38)	234	137 (44.5)	208	137 (44.7)	207
IP	14.7 (6.72)	118	14.8 (6.78)	118	93.0 (33.2)	180	93.2 (33.4)	179

The PS derived C_w for Galway and Dublin were determined by the MI and (in parenthesis), the Reference laboratory.

The majority of the Galway PCB water concentrations (seven out of twelve), and all of the Dublin PCB water concentrations determined by the MI (using either Log $K_{sr,w}$ value) are higher than those determined by the reference laboratory (*Table 4.9*). The PAH concentrations as reported by the MI for both sites are consistently higher than those reported by the Reference, with acenapthene being the only exception (*Table 4.10*).

The water concentrations determined by the two laboratories from the duplicate Galway PS membranes are similar in 7 of the 12 PCB compounds, i.e. PCBs 18, 28, 52, 138, 153, 170 and 180, with MI concentrations ranging from 12.3 % less than, to 37.1 % greater than the Reference laboratory values). The PCB with the most noticeable percentage difference is PCB 31, where the MI concentrations are 749 % (Yates et al) and 775 % (Smedes) greater than the Reference laboratory values. This discrepancy may be accounted for by way of co-elution of compounds in the analysis carried out by the MI.

In general, the percentage differences arising from the comparison of the Dublin PS derived PCB water concentrations as determined by the MI and the Reference laboratory are considerably greater than those in Galway. As regards the PAH concentrations (*Table 4.10*), the percentage differences tend to increase with molecular weight, with the Dublin percentages being generally greater than those observed at the Galway site.

4.2.5 The Effects of Altering the Sampling Rate (R_S)

The R_S values determined by the MI for both Galway and Dublin are lower than those determined by the Reference Laboratory. While the Galway R_S values determined by both laboratories are relatively close (Galway 8.48 l/d (MI); 10.2 l/d (Ref), the Dublin R_S determined by the MI (2.38 l/d) is almost half that determined by the Reference laboratory (4.93 l/d).

In order to assess the effect of such a variation in R_S values, the following investigation were undertaken. The water concentration for PCB 18 as determined by the MI for the Dublin site, using the true R_S of 2.38 l/d, results in a water concentration of 31.9 pg/l. All parameters remaining constant (membrane weight *etc*.), bar the doubling of the R_S (Fictional R_S: 4.76 l/d), results in a water concentration of 17.4 pg/l. Thus, all other parameters remaining constant in *Eqn. 3.7*, the effect of halving the R_S results in the doubling of the resultant water concentration value. Therefore, had the membrane concentrations determined by both laboratories for Dublin been the exact same (in reality they are similar for majority of PCBs (*Table 4.4*)), but each used their own R_S in the determination of the PS derived water concentrations, the resultant water concentrations for the MI would be approximately double that of the Reference laboratory (This is generally true for the majority of the Dublin PCBs in *Table 4.7*). It

thus follows that the majority of the percentage difference observed in the water concentrations as determined by the two laboratories for the Dublin Site is due to the large variation of the R_S values. The above investigation also relates to the Dublin PAH concentrations as they too were determined using the same sampling rates as for PCB determinations.

4.3 Evaluation of the Influence of using either Literature or Estimated Log $K_{sr,w}$ Values on MI PS derived PCB and PAH C_w

As previously discussed MI analytical results form the basis of this thesis. Data obtained from the passive sampling membranes was subsequently converted into passive sampling derived water concentrations (*Tables 4.13 - 4.15*) using literature (where available) and estimated Log $K_{sr,w}$ values (*Table 3.7*). To date this thesis has not addressed the degree to which water concentrations derived from literature Log $K_{sr,w}$ values differ from those derived using Log $K_{sr,w}$ values modelled/estimated during the course of this work. This section thus evaluates the influence of using either literature or estimated Log $K_{sr,w}$ values on passive sampling derived PCB and PAH water concentrations.

Passive sampling derived water concentrations determined using available Log $K_{sr,w}$ values differ from those determined using estimated Log $K_{sr,w}$ values (See *Tables 4.13 - 4.15*). The degree to which the two techniques differ for dissolved PCB and PAH compounds at each of the test sites is reported in *Table 4.11* and *Table 4.12*.

There are no literature Log $K_{sr,w}$ values available for a variety of PCB compounds (PCB 18, 33, 41, 47, 51, 56/60, 61, 66, 77, 81, 87, 114, 123, 126, 129, 141, 167, 169, 185, 191, 193, 194, 201, 202, 203, 206, 208) and PAHs (chrysene–triphenylene, benzo[b]naphtho[2,1-d]thiophene, benzo[ghi]fluoranthene, anthanthrene and coronene), therefore the PS derived water concentrations for such compounds were determined using estimated Log $K_{sr,w}$ values only.

As this Section discusses the percentage differences arising from the determination of PS derived water concentrations using literature Log $K_{sr,w}$ values or estimated Log $K_{sr,w}$ values, those afore mentioned compounds (having PS derived C_w determined from estimated values only) have been omitted from the tables and discussion below.

Table 4.11: Percentage difference in PS derived PCB water concentrations determined using estimated and (literature) Log $K_{sr,w}$ values for both test locations

Sample Type (Unit)	**PS derived C_w (pg/l)**			
Location	**Galway**		**Dublin**	
	MI	**% difference**	**MI**	**% difference**
PCB 105	0.47 (0.47)	-1.27	4.56 (4.57)	-0.38
PCB 118*	1.36 (1.35)	0.14	12.5 (12.4)	0.04
PCB 156	<0.07 (<0.07)	0.21	0.58 (0.58)	0.06
PCB 157	<0.25 (<0.25)	-0.52	<0.56 (<0.56)	-0.15
PCB 189	<0.11 (<0.11)	-0.25	<0.28 (<0.28)	-0.07
PCB 28	6.33 (6.56)	-3.52	40.3 (40.7)	-1.08
PCB 52	5.87 (5.94)	-1.17	45.4 (45.6)	-0.35
PCB 101	3.51 (3.48)	0.81	27.3 (27.2)	0.24
PCB 118*	1.36 (1.35)	0.14	12.5 (12.4)	0.04
PCB 138	1.85 (1.85)	0.33	10.7 (10.7)	0.10
PCB 153	1.93 (1.93)	0.04	7.58 (7.58)	0.01
PCB 180	0.40 (0.40)	-0.05	1.70 (1.70)	-0.02
PCB 31	18.9 (20.6)	-8.00	79.3 (81.4)	-2.51
PCB 44	1.92 (1.86)	3.18	19.8 (19.6)	0.94
PCB 49	2.47 (2.43)	1.37	20.4 (20.3)	0.41
PCB 74	<0.37 (<0.37)	-1.65	<1.13 (<1.13)	-0.49
PCB 99	1.29 (1.29)	-0.04	8.38 (8.39)	-0.01
PCB 110	1.58 (1.59)	-0.18	22.6 (22.6)	-0.05
PCB 128	<0.36 (<0.36)	0.05	1.49 (1.49)	0.01
PCB 149	1.31 (1.31)	0.31	7.53 (7.52)	0.09
PCB 151	0.47 (0.47)	0.22	1.84 (1.84)	0.06
PCB 170	<0.36 (<0.36)	-0.04	<1.12 (<1.12)	-0.01
PCB 183	<0.36 (<0.36)	0.05	<1.12 (<1.12)	0.02
PCB 187	1.35 (1.35)	0.04	3.83 (3.83)	0.01
PCB 209	1.18 (1.18)	0.01	3.26 (3.26)	0.002

As the concentration differences are not always visible on a three significant figure basis, the differences are presented on a percentage difference basis.

The majority of differences between the PCB water concentrations derived using estimated Log $K_{sr,w}$ and those derived using literature values were found to be in the order of <1 % (pg/l). The greatest percentage difference observed between the PCB water concentrations determined using estimated and literature Log $K_{sr,w}$ values for both sites, was for PCB 31. The concentrations determined for this compound using the estimated Log $K_{sr,w}$ value is lower than that determined using the available Log $K_{sr,w}$ value by 8 % (Galway) and 2.51 % (Dublin). The estimated Log $K_{sr,w}$ value was found

to result in a lower water concentration for half the PCBs (105, 157, 189 28, 52, 180, 31, 74, 99, 110 and 170), (maximum difference 8.00 % for PCB 31) while use of estimated Log $K_{sr,w}$ values resulted in higher water concentration for the remaining PCBs (maximum difference 3.18 % for PCB 44).

Table 4.12: Percentage difference in PS derived PAH water concentrations determined using estimated and (literature) Log $K_{sr,w}$ values for both test locations

Sample Type (Unit)	PS derived C_w (ng/l)			
Location	**Galway**		**Dublin**	
	MI	**% difference**	**MI**	**% difference**
Naphthalene	28.5 (11.7)	144	12.6 (6.39)	97.1
Acenaphthylene	0.91 (0.93)	-2.10	2.55 (2.59)	-1.50
Acenaphthene	0.47 (0.36)	29.4	2.17 (1.94)	12.3
Fluorene	1.91 (2.16)	-11.5	8.62 (9.04)	-4.70
Phenanthrene	5.33 (6.01)	-11.3	18.4 (19.1)	-3.96
Anthracene	0.41 (0.40)	2.42	1.48 (1.47)	0.79
Fluoranthene	3.16 (3.89)	-18.7	12.4 (13.2)	-6.20
Pyrene	2.58 (2.94)	-12.2	14.6 (15.2)	-3.95
Benzo[a]anthracene	0.25 (0.25)	-1.51	1.56 (1.56)	-0.45
Benzo[b+j+k]fluoranthene	0.24 (0.24)	1.23	1.18 (1.17)	0.36
Benzo[a]pyrene	0.07 (0.07)	0.20	0.38 (0.38)	0.06
Indeno[1,2,3-cd]pyrene	0.01 (0.01)	0.004	0.09 (0.09)	0.001
Benzo[ghi]perylene	0.03 (0.03)	-0.02	0.14 (0.14)	-0.005
Dibenz[ah]anthracene	0.02 (0.02)	0.12	0.05 (0.05)	0.03
Benzo[c]phenanthrene	0.13 (0.13)	-1.09	0.45 (0.45)	-0.32
Benzo[e]pyrene	0.08 (0.08)	-0.13	0.52 (0.52)	-0.04

As the concentration differences are not always visible on a three significant figure basis, the differences are presented on a percentage difference basis.

On comparison of the PAH water concentrations determined using estimated and actual Log $K_{sr,w}$ values, naphthalene appears to have the greatest percentage difference for both sites. The concentration determined for naphthalene using the estimated Log $K_{sr,w}$ value is greater than that determined using the available literature Log $K_{sr,w}$ value by 144 % (Galway) and 97.1 % (Dublin). Acenaphthene follows, with percentages of 29.4 and 12.3 for Galway and Dublin respectively. Fluoranthene is next in relation to percentage differences, however, the concentration determined using the estimated Log $K_{sr,w}$ value for this compound is lower than that determined using the available Log $K_{sr,w}$ value by 18.7 % (Galway) and 6.20 % (Dublin). Fluorene, phenanthrene and pyrene have similar differences, (-11.3 to -12.2: Galway; -3.95 to -4.70: Dublin), while the remaining differences were between -2.1 and 1.23 %.

Greater differences were observed for PAHs compared to PCBs, however the extent of these differences was generally found to be acceptable (exception: naphthalene and acenaphthene). The use of estimated $K_{sr,w}$ values was found to be prone to greatest error for lower Log K_{ow} ($K_{sr,w}$) PAHs, especially for naphthalene and acenaphthene. Overall the use of either literature or estimated/modelled $K_{sr,w}$ values was found to be suitable for the derivation of passive sampling water concentrations for the majority of PCBs and higher condensed PAHs.

4.4 Introduction to the Means of Assessing Test Mussel Tissue Concentrations and the C_w as determined from the "Spot" Water Samples and the Silicone Rubber PS

While mussel tissue data are presented and discussed later, the main focus of this Chapter is to enable the comparison of contaminant concentrations determined from the spot water samples and the PS membranes. In order for contaminant concentrations as determined from the two Irish test locations to be compared, they must first be presented on a similar concentration basis (as described in Section 3.8).

This is a relatively straight forward process for spot water results as they are reported in the correct format (pg/l or ng/l). As contaminants concentrations in the spot water samples are compared to those derived from the passive sampling devices, final derived water concentrations from each matrix were calculated and reported in *Tables 4.13 – 4.15* below. For each of the summary tables:

- The first reported value for PS derived C_w use estimated Log $K_{sr,w}$ for all compounds, with figures in parenthesis reporting the dissolved water concentration as determined using literature Log $K_{sr,w}$ values.

Table 4.13: The WHO and Marker PCB dissolved C_w (pg/l), as determined by the spot water samples and the PS membranes taken at both test locations

	Sample Type (Unit)	Spot (pg/l)		PS derived C_w (pg/l)	
	Location	**Galway**	**Dublin**	**Galway**	**Dublin**
12 WHO PCBs	**PCB 77**	44.3	<26.0	<0.16	1.31
	PCB 81	0.91	<0.50	0.08	0.19
	PCB 126	15.7	<7.00	0.08	0.29
	PCB 169	0.35	<0.50	0.03	0.09
	PCB 105	33.6	<37.0	0.47 (0.47)	4.56 (4.57)
	PCB 114	<3.00	<4.00	<0.09	<0.34
	PCB 118*	202	<90.0	1.36 (1.35)	12.5 (12.4)
	PCB 123	10.7	<9.00	0.15	0.93
	PCB 156	22.1	<14.0	<0.07 (<0.07)	0.58 (0.58)
	PCB 157	<62.0	<47.0	<0.25 (<0.25)	<0.56 (<0.56)
	PCB 167	16.3	<11.0	<0.09	0.54
	PCB 189	<3.00	<3.00	<0.11 (<0.11)	<0.28 (<0.28)
7 Marker PCBs	**PCB 28**	646	<400	6.33 (6.56)	40.3 (40.7)
	PCB 52	<70.0	<60.0	5.87 (5.94)	45.4 (45.6)
	PCB 101	290	<200	3.51 (3.48)	27.3 (27.2)
	PCB 118*	202	<90.0	1.36 (1.35)	12.5 (12.4)
	PCB 138	432	<200	1.85 (1.85)	10.7 (10.7)
	PCB 153	420	<200	1.93 (1.93)	7.58 (7.58)
	PCB 180	73.4	<60.0	0.40 (0.40)	1.70 (1.70)

*PCB 118 included twice as it is both a WHO and a marker PCB.

Table 4.14: "Other" PCB dissolved C_w (pg/l), as determined by the spot water samples and PS membranes taken at both test locations

	Sample Type (Unit)	Spot (pg/l)		PS derived C_w (pg/l)	
	Location	**Galway**	**Dublin**	**Galway**	**Dublin**
Other PCBs	**PCB 18**	213	<200	3.73	31.9
	PCB 31	415	<200	18.9 (20.6)	79.3 (81.4)
	PCB 33	431	<300	702	2,327
	PCB 41	86.0	<80.0	72.8	224
	PCB 44	<40.0	<40.0	1.92 (1.86)	19.8 (19.6)
	PCB 47	69.6	<60.0	12.4	54.8
	PCB 49	49.5	<40.0	2.47 (2.43)	20.4 (20.3)
	PCB 51	<20.0	<20.0	51.2	163
	PCB 56/60	178	<100	3.66	30.2
	PCB 61	51.0	<30.0	0.83	8.61
	PCB 66	88.3	<60.0	1.54	15.8
	PCB 74	<20.0	<20.0	<0.37 (<0.37)	<1.13 (<1.13)
	PCB 87	66.4	<40.0	8.11	32.1
	PCB 99	<20.0	<20.0	1.29 (1.29)	8.38 (8.39)
	PCB 110	201	<90.0	1.58 (1.59)	22.6 (22.6)
	PCB 128	39.5	<20.0	<0.36 (<0.36)	1.49 (1.49)
	PCB 129	<20.0	<20.0	<0.36	<1.12
	PCB 141	76.6	<50.0	<0.36	<1.12
	PCB 149	205	<100	1.31 (1.31)	7.53 (7.52)
	PCB 151	<40.0	<30.0	0.47 (0.47)	1.84 (1.84)
	PCB 170	<30.0	<30.0	<0.36 (<0.36)	<1.12 (<1.12)
	PCB 183	36.9	<20.0	<0.36 (<0.36)	<1.12 (<1.12)
	PCB 185	<20.0	<20.0	<0.36	<1.12
	PCB 187	37.7	<30.0	1.35 (1.35)	3.83 (3.83)
	PCB 191	<20.0	<20.0	<0.36	<1.12
	PCB 193	<20.0	<20.0	<0.36	<1.12
	PCB 194	<20.0	<20.0	<0.36	<1.12
	PCB 201	<20.0	<20.0	<0.36	<1.12
	PCB 202	<20.0	<20.0	<0.36	<1.12
	PCB 203	<20.0	<20.0	<0.36	<1.12
	PCB 206	<20.0	<20.0	<0.36	<1.12
	PCB 208	<20.0	<20.0	<0.36	<1.12
	PCB 209	<20.0	<20.0	1.18 (1.18)	3.26 (3.26)

Table 4.15: PAH dissolved water concentrations (ng/l), as determined by the spot water samples and passive sampling membranes taken at both test locations

	Sample Type (Unit)	Spot (ng/l)		PS derived C_w (ng/l)	
	Location	**Galway**	**Dublin**	**Galway**	**Dublin**
US EPA PAHs	Naphthalene (N)	9.79	7.91	28.5 (11.7)	12.6 (6.39)
	Acenaphthylene (Acy)	0.76	1.29	0.91 (0.93)	2.55 (2.59)
	Acenaphthene (Ace)	1.63	1.76	0.47 (0.36)	2.17 (1.94)
	Fluorene (F)	2.08	5.82	1.91 (2.16)	8.62 (9.04)
	Phenanthrene (P)	<5.00	9.39	5.33 (6.01)	18.4 (19.1)
	Anthracene (A)	0.96	1.35	0.41 (0.40)	1.48 (1.47)
	Fluoranthene (Fl)	<2.00	4.17	3.16 (3.89)	12.4 (13.2)
	Pyrene (Py)	<2.00	6.33	2.58 (2.94)	14.6 (15.2)
	Benzo[a]anthracene (BaA)	0.24	2.15	0.25 (0.25)	1.56 (1.56)
	Chrysene - Triphenylene* (C-T)	<0.70	2.75	1.04	4.29
	Benzo[b+j+k]fluoranthene (BbjkF)	0.75	6.92	0.24 (0.24)	1.18 (1.17)
	Benzo[a]pyrene (BaP)	0.70	2.29	0.07 (0.07)	0.38 (0.38)
	Indeno[1,2,3-cd]pyrene (IP)	0.41	2.19	0.01 (0.01)	0.09 (0.09)
	Benzo[ghi]perylene (BghiP)	<0.40	2.30	0.03 (0.03)	0.14 (0.14)
	Dibenz[ah]anthracene (DahA)	<0.60	0.35	0.02 (0.02)	0.05 (0.05)
Other PAHs	Benzo[b]naphtho [2,1-d] thiophene (BbN)	0.08	0.82	0.06	0.38
	Benzo[c]phenanthrene (BcP)	0.15	0.74	0.13 (0.13)	0.45 (0.45)
	Benzo[ghi]fluoranthene (BghiF)	0.23	0.54	0.17	0.62
	Benzo[e]pyrene (BeP)	0.60	3.38	0.08 (0.08)	0.52 (0.52)
	Anthanthrene (An)	<0.80	<0.20	<0.03	<0.05
	Coronene (Co)	0.21	0.86	<0.05	<0.04
PAH Ratios	P/A		6.98	13.0 (15.0)	12.4 (13.0)
	Fl/Py		0.66	1.22 (1.32)	0.85 (0.87)
	A/178		0.13	0.07 (0.06)	0.07 (0.07)
	BaA/228		0.44	0.19	0.27
	Fl/(Fl+Py)		0.40	0.55 (0.57)	0.46 (0.46)
	IP/(IP+BghiP)		0.49	0.25 (0.25)	0.39 (0.39)

PAH ratios as follows: P/A: phenanthrene/anthracene; Fl/Py: fluoranthene/pyrene; A/178: anthracene/anthracene + phenanthrene; BaA/228: benzo[a]anthracene/benzo[a]anthracene + chrysene; Fl/Fl + Py: fluoranthene/fluoranthene + pyrene; IP/IP + BghiP: indeno[1,2,3-c,d]pyrene/indeno[1,2,3-c,d]pyrene + benzo[g,h,i]perylene.

The means of assessing the dissolved water contaminant concentration shown previously in the Summary Tables are as follows:

4.4.1 Contaminant Concentrations in the Spot Water Samples

4.4.2 PS derived Contaminant C_w determined using a Combination of Literature and Estimated Log $K_{sr,w}$ Values

4.4.1 Contaminant Concentrations in the Spot Water Samples

The spot water samples were tested as total unfiltered water, thus the suspended particular matter content of the water is an important factor in attempting to understand the contaminant concentrations. The suspended solids at the Dublin site (20.6 mg/l)

were approximately 4 times greater than that at the Galway site (5 mg/l). It should be noted that suspended solids were relatively low at both sites and at these levels their presence is not expected to unduly affect total "dissolved" results. No PCB compounds were detected in the Dublin spot water sample i.e. all concentrations fell below the LoQ values; therefore an assessment of PCB levels was only possible in the Galway sample.

Owing to the hydrophobic nature of PCBs and PAHs, their distribution in the water column is governed by water solubility and associated partitioning properties, represented by the octanol-water partition co-efficient K_{ow} (See *Table 3.7* for Log K_{ow} values). In general there is an inverse relationship between K_{ow} and water solubility of a compound [15]. As the K_{ow} increases, the tendency of the hydrophobic contaminant to associate itself with organic matter also increases. The target analytes in this study (PCBs and PAHs) have relatively low water solubilities (solubility generally decreases with increasing molecular size) and therefore they tend to associate themselves with the available organic matter (including sediment, plankton and particulates) [16].

4.4.2 PS derived Contaminant C_w determined using a Combination of Literature and Estimated Log $K_{sr,w}$ Values

As discussed previously (See Section 4.3), the use of silicone passive sampling technologies in conjunction with literature or estimated/modelled $K_{sr,w}$ values provides a useful tool for the determination of trace levels of dissolved PCBs and PAHs in the water column.

As the majority of compounds tested in this study have available literature Log $K_{sr,w}$ values (24 PCBs and 16 PAHs), these values were used in the final determination of the PS derived water concentrations as reported in this present study. For the remaining

compounds, estimated Log $K_{sr,w}$ values are used. Such estimated values are generally considered reliable (See Section 4.3) in the absence of literature values, given that the percentage differences between actual and estimated concentrations shown in *Table 4.11* and *Table 4.12* were within an acceptable range (exception: naphthalene and acenaphthene).

The application of the technique using PS derived water concentration data from the MI is further discussed in Sections 4.5.3 and 4.6.3 whereby the PCB and PAH water concentrations were determined using a combination of both literature (where available) and estimated Log $K_{sr,w}$ values. *Tables 4.13 - 4.15* document the concentration data used to derive graphical outputs as reported in such Sections.

The contaminant concentrations as determined during the course of this study, i.e. PCB and PAH mussel tissue concentrations and the dissolved PCB and PAH water concentrations (as determined from the "spot" water samples and PS membranes) are assessed in the following Sections:

4.5. Assessment of PCB Concentrations in Various Media

4.6. Assessment of PAH Concentrations in Various Media

4.5 Assessment of PCB Concentrations in Various Media

The concentrations of PCBs detected in the tissues of the test mussels are detailed in Section 4.5.1 (expressed on both a dry weight basis and a lipid normalised dry weight basis (See *Table 4.16*)), while the dissolved PCB water concentrations (See *Table 4.13* and *Table 4.14*) are assessed as follows:

4.5.2 Assessment of PCBs in the Spot water samples.

4.5.3 Passive sampling derived PCB water concentrations.

4.5.1 Assessment of PCB Concentrations in Study Mussels

As a consequence of the number of PCBs (n=51) analysed in test mussels at both Galway and Dublin, reporting of results was divided into a number of Sections;

4.5.1.1 Assessment of WHO PCBs in test mussels

4.5.1.2 Assessment of Marker PCBs in test mussels

4.5.1.3 Assessment of "other" PCBs in test mussels.

Each of the PCB groupings are further discussed below. It should be noted that of a total of 51 PCBs analysed that PCB 74 was the only congener not detected in any of the mussel samples.

Concentrations of PCBs in test mussels are reported in *Table 4.16* on a dry weight and dry weight lipid normalised (in parenthesis) basis. However, only the dry weight tissue concentrations are used for graphical purposes.

Table 4.16: PCB concentrations µg/kg dry weight and in parenthesis (µg/kg dry weight and lipid normalised) in test site mussel samples

	Sample Type	Mussel (ug/kg)				
	Location	Galway		Dublin		
		T(start)	T(end)	T(start)	T(end)	Native NBL
12 WHO PCBs	PCB 77	0.02 (0.02)	0.03 (0.02)	0.09 (0.07)	0.09 (0.08)	0.22 (0.11)
	PCB 81	0.001 (0.001)	0.002 (0.001)	0.005 (0.004)	0.005 (0.004)	0.01 (0.01)
	PCB 126	0.004 (0.003)	0.006 (0.004)	0.007 (0.01)	0.008 (0.01)	0.02 (0.01)
	PCB 169	0.001 (0.001)	0.001 (0.001)	0.001 (0.001)	0.001 (0.001)	0.001 (0.001)
	PCB 105	0.15 (0.12)	0.14 (0.10)	0.74 (0.62)	0.89 (0.74)	1.59 (0.79)
	PCB 114	0.006 (0.005)	0.005 (0.004)	0.03 (0.03)	0.03 (0.02)	0.06 (0.03)
	PCB 118	0.63 (0.48)	0.48 (0.34)	1.89 (1.58)	2.47 (2.04)	4.53 (2.24)
	PCB 123	0.09 (0.07)	0.05 (0.04)	0.12 (0.10)	0.13 (0.11)	0.26 (0.13)
	PCB 156	0.06 (0.05)	0.06 (0.04)	0.18 (0.15)	0.21 (0.17)	0.36 (0.18)
	PCB 157	0.01 (0.01)	0.01 (0.01)	0.05 (0.04)	0.06 (0.05)	0.10 (0.05)
	PCB 167	0.05 (0.04)	0.05 (0.03)	0.10 (0.08)	0.13 (0.11)	0.24 (0.12)
	PCB 189	0.007 (0.01)	0.007 (0.005)	0.01 (0.01)	0.01 (0.01)	0.02 (0.01)
7 Marker PCBs	PCB 28	<0.46 (<0.35)	0.47 (0.34)	<0.42 (<0.35)	<0.42 (<0.35)	1.25 (0.62)
	PCB 52	0.11 (0.08)	0.28 (0.20)	1.14 (0.95)	1.16 (0.96)	2.83 (1.40)
	PCB 101	1.42 (1.09)	0.94 (0.67)	2.63 (2.19)	2.77 (2.29)	5.96 (2.95)
	PCB 118	0.63 (0.48)	0.48 (0.34)	1.89 (1.58)	2.47 (2.04)	4.53 (2.24)
	PCB 138	1.84 (1.41)	1.43 (1.02)	2.76 (2.30)	3.29 (2.72)	6.11 (3.03)
	PCB 153	1.99 (1.53)	1.67 (1.19)	2.44 (2.03)	2.97 (2.45)	5.73 (2.84)
	PCB 180	0.36 (0.28)	0.28 (0.20)	0.38 (0.31)	0.39 (0.32)	0.86 (0.43)
Other PCBs	PCB 18	<0.20 (<0.15)	<0.23 (<0.16)	<0.24 (<0.20)	<0.24 (<0.20)	0.47 (0.23)
	PCB 31	<0.26 (<0.20)	<0.38 (<0.27)	<0.36 (<0.30)	<0.36 (<0.30)	0.90 (0.45)
	PCB 33	<0.26 (<0.20)	0.37 (0.26)	<0.30 (<0.25)	<0.36 (<0.30)	0.50 (0.25)
	PCB 41	0.11 (0.09)	0.26 (0.19)	0.70 (0.58)	0.77 (0.63)	1.80 (0.89)
	PCB 44	0.07 (0.05)	0.17 (0.12)	0.49 (0.41)	0.49 (0.41)	1.20 (0.59)
	PCB 47	<0.07 (<0.05)	0.20 (0.14)	0.37 (0.31)	0.38 (0.31)	1.04 (0.52)
	PCB 49	0.07 (0.05)	0.18 (0.13)	0.59 (0.49)	0.60 (0.50)	1.54 (0.76)
	PCB 51	<0.007 (<0.01)	0.02 (0.01)	0.03 (0.02)	0.03 (0.02)	0.07 (0.04)
	PCB 56/60	0.46 (0.35)	0.45 (0.32)	1.54 (1.29)	1.62 (1.34)	3.79 (1.88)
	PCB 61	0.09 (0.07)	0.11 (0.08)	0.44 (0.37)	0.48 (0.40)	1.25 (0.62)
	PCB 66	0.22 (0.17)	0.24 (0.17)	0.91 (0.76)	1.01 (0.83)	2.41 (1.19)
	PCB 74	<0.01 (<0.01)	<0.02 (<0.01)	<0.04 (<0.03)	<0.05 (<0.05)	<0.09 (<0.05)
	PCB 87	0.33 (0.25)	0.16 (0.12)	0.78 (0.65)	0.86 (0.71)	1.87 (0.93)
	PCB 99	0.24 (0.18)	0.24 (0.17)	0.90 (0.75)	0.99 (0.82)	2.04 (1.01)
	PCB 110	0.71 (0.55)	0.33 (0.23)	1.60 (1.33)	1.70 (1.41)	3.68 (1.82)
	PCB 128	0.16 (0.12)	0.13 (0.09)	0.42 (0.35)	0.47 (0.39)	0.88 (0.44)
	PCB 129	<0.02 (<0.02)	<0.02 (<0.01)	<0.02 (<0.01)	<0.02 (<0.02)	0.03 (0.02)
	PCB 141	0.31 (0.24)	0.15 (0.11)	0.05 (0.04)	0.04 (0.03)	0.19 (0.10)
	PCB 149	1.66 (1.28)	1.06 (0.76)	1.60 (1.33)	1.83 (1.51)	3.52 (1.74)
	PCB 151	0.55 (0.42)	0.32 (0.23)	0.39 (0.32)	0.44 (0.36)	0.88 (0.44)
	PCB 170	0.10 (0.08)	0.06 (0.04)	0.06 (0.05)	0.05 (0.04)	0.20 (0.10)
	PCB 183	0.37 (0.28)	0.32 (0.23)	0.35 (0.29)	0.43 (0.36)	0.86 (0.43)
	PCB 185	0.03 (0.02)	0.02 (0.01)	0.007 (0.01)	0.008 (0.01)	0.02 (0.01)
	PCB 187	0.77 (0.59)	0.78 (0.56)	0.89 (0.74)	1.07 (0.88)	1.97 (0.98)
	PCB 191	0.008 (0.01)	0.006 (0.005)	0.006 (0.005)	0.007 (0.01)	0.02 (0.01)
	PCB 193	0.03 (0.02)	0.02 (0.01)	0.02 (0.02)	0.02 (0.02)	0.04 (0.02)
	PCB 194	0.02 (0.01)	0.01 (0.01)	0.03 (0.02)	0.03 (0.02)	0.04 (0.02)
	PCB 201	0.03 (0.02)	0.02 (0.01)	0.01 (0.01)	0.01 (0.01)	0.04 (0.02)
	PCB 202	0.11 (0.09)	0.12 (0.09)	0.14 (0.12)	0.18 (0.15)	0.28 (0.14)
	PCB 203	0.04 (0.03)	0.04 (0.03)	0.06 (0.05)	0.06 (0.05)	0.10 (0.05)
	PCB 206	<0.003 (<0.003)	<0.004 (<0.003)	0.005 (0.005)	0.005 (0.004)	0.007 (0.003)
	PCB 208	<0.003 (<0.002)	<0.003 (<0.002)	<0.002 (<0.002)	<0.002 (<0.002)	0.002 (0.001)
	PCB 209	<0.004 (<0.003)	<0.005 (<0.004)	0.005 (0.005)	<0.004 (<0.003)	<0.004 (<0.002)

4.5.1.1 Assessment of WHO PCBs in Test Mussels

Due to the large variation in WHO PCB concentrations encountered in the mussel samples, analytical results were sub-divided into two groups for graphical presentation. The concentrations of the two most abundant WHO PCBs (i.e. PCB 105 and 118) are presented in *Fig. 4.3a*, while the remaining PCBs in this category are presented in *Fig. 4.3b*.

The general trend for the WHO PCBs in all samples, arranged in order of decreasing concentration, is as follows: 118>105>156>123>167>77>157. This order shifts slightly for the Dublin T(end) sample, in that the concentration of PCB 167>123, by 0.005 µg/kg dry weight.

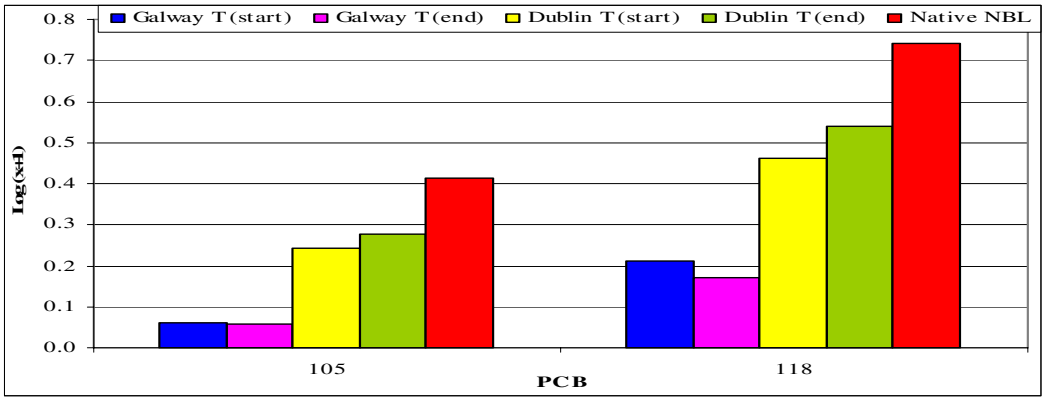

Figure 4.3a: Concentrations (µg/kg dry weight) (Log(x+1)) of two most abundant WHO PCBs in all mussel samples taken from the Galway and Dublin sites.

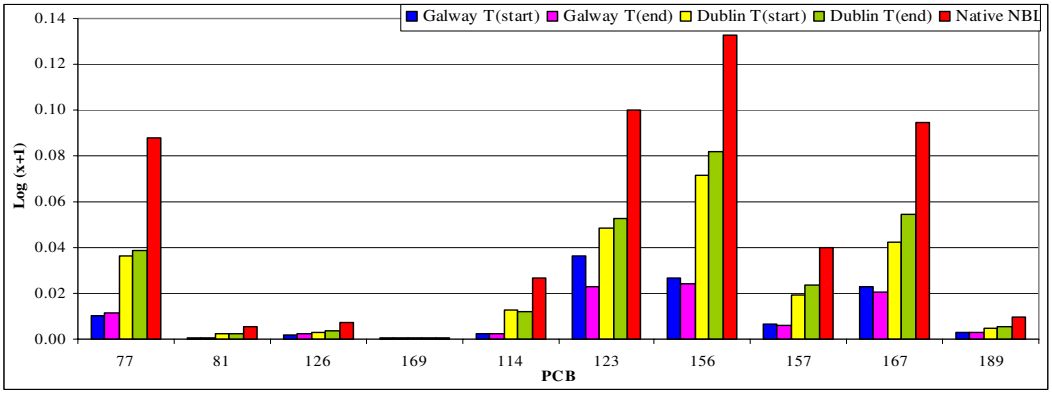

Figure 4.3b: Concentrations (µg/kg dry weight) (Log(x+1)) of remaining ten WHO PCBs in all mussel samples taken from the Galway and Dublin sites.

4.5.1.1.1 Assessment of WHO PCBs in Galway Mussels

Concentrations for eight of the twelve WHO PCBs decreased in the Galway mussels during the 6 week deployment period, with only a slight increase in concentration for PCB 77, PCB 81, PCB 126 and PCB 169. Some of the increases/decreases were found to be of the order of 0.0001 µg/kg, and are thus not visible from *Table 4.16* (as concentrations are presented on a three and four significant figure basis). Many such increases/decreases would be expected to be within the uncertainty of the test method (analytical error) and would not be significant.

4.5.1.1.2 Assessment of WHO PCBs in Dublin Mussels

During the initial "equilibration" period (t=26 days), all WHO PCB concentrations increased at the NBL, indicating either greater bioavailability or contaminant levels. Concentrations of WHO PCBs in the Dublin T(start) mussels continued to increase during the 6 week PS deployment period. However, the rate of increase was not as rapid as during the original 26 day equilibration previously mentioned. Concentrations of WHO PCBs were found to be greatest in the native NBL mussels collected at the end of the exposure study.

4.5.1.2 Assessment of Marker PCBs in Test Mussels

Due to the smaller number of compounds in this group and narrower concentration ranges, results for all mussel samples have been represented on a single graph (*Fig. 4.4*). PCB 28 was not detected in the Galway T(start), Dublin T(start) or Dublin T(end) mussel samples. Elevated LoQs for PCB 28 (0.42 to 0.46 µg/kg dry weight) were however determined for these samples (See *Table 4.16*).

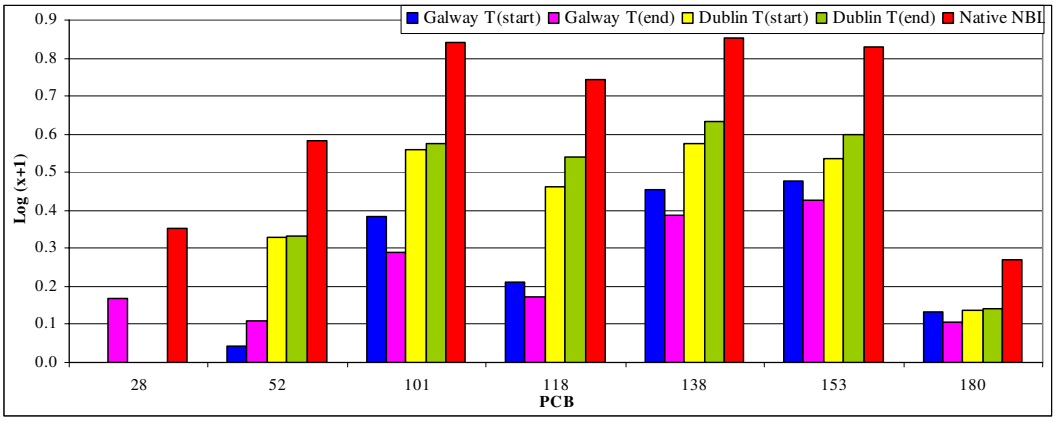

Figure 4.4: Concentrations (µg/kg dry weight) (Log(x+1)) of the Marker PCBs in all mussel samples taken from the Galway and Dublin sites.

4.5.1.2.1 Assessment of Marker PCBs in Galway Mussels

Concentrations of the two lowest chlorinated marker PCBs (PCB 28 and PCB 52) were greater in the Galway T(end) mussels than in the Galway T(start) sample. The reverse was true for the remaining five marker PCBs, indicating that the level of these compounds in the mussel tissues decreased during the deployment period. While this may potentially indicate an ability for the mussels to metabolise/deplete/excrete these PCBs from their tissues during the deployment period, it would require further investigation.

4.5.1.2.2 Assessment of Marker PCBs in Dublin Mussels

PCB 28 was not detected (high LoQ 0.42 to 0.46 µg/kg dry weight) in either the Galway T(start) mussels or in the equilibrated mussels (Dublin T(start) sample). The concentrations of the remaining six marker PCBs increased during the 26 day equilibration period of the Galway T(start) mussels at the Northbank Lighthouse, potentially indicating greater bioavailability and/or concentrations at the Dublin site.

Increases in marker PCB concentrations were observed during the 6 week deployment period for the remaining 6 marker PCBs at the Dublin site, with concentrations of PCBs 118, 138 and 153 increasing by over 0.5 µg/kg dry weight. The full range of marker PCBs were determined in the native NBL mussel, and concentrations were the highest of all mussel samples. The seven PCBs in the Native NBL sample were arranged in order of decreasing concentration: PCB 138>101>153>118>52>28>180.

4.5.1.3 Assessment of "Other" PCBs in Test Mussels

A large number of "other" PCBs (n=33) were measured in this grouping, therefore where a compound was not detected (i.e. the concentration fell below the LoQ), the relevant LoQs are reported in *Table 4.16* but the compounds were omitted from the graphical representation of results.

4.5.1.3.1 Assessment of "Other" PCBs in Galway Mussels

PCBs 18, 31, 129, 206, 208 and 209 were not detected in either of the Galway mussel samples (T(start) and/or T(end)), with PCB 33, 47 and 51 not detected in Galway T(start). The Galway T(end) mussel sample was found to have higher concentrations of the less chlorinated PCBs, while the T(start) sample has a better representation of the mid range chlorinated compounds. The concentrations of the highly chlorinated compounds were comparable (See *Fig. 4.5*).

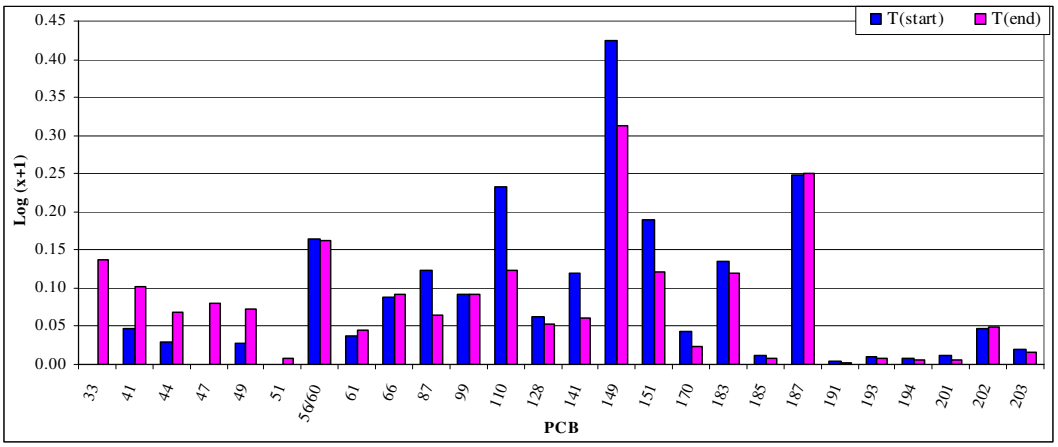

Figure 4.5: PCB concentrations (µg/kg dry weight) (Log(x+1)) in T(start) and T(end) mussel samples taken from the Galway site.

4.5.1.3.2 Assessment of "Other" PCBs in Dublin Mussels

Concentrations of the lower chlorinated PCBs increased during the 26 day equilibration period of the Galway T(start) mussels at the NBL, with some of the compounds more than tripling in concentration (See *Fig. 4.6*). This indicates either increased bioavailability/concentration of such contaminants at the Dublin site. The more chlorinated compounds (i.e. from Hexa PCBs upwards) have higher or equal concentrations in the equilibrated mussels (Dublin T(start) sample). PCBs 18, 31, 33, 129 and 208 were not detected in either of the T(start) mussel samples, with PCBs 47, 51, 206 and 209 not detected in the Galway T(start) sample.

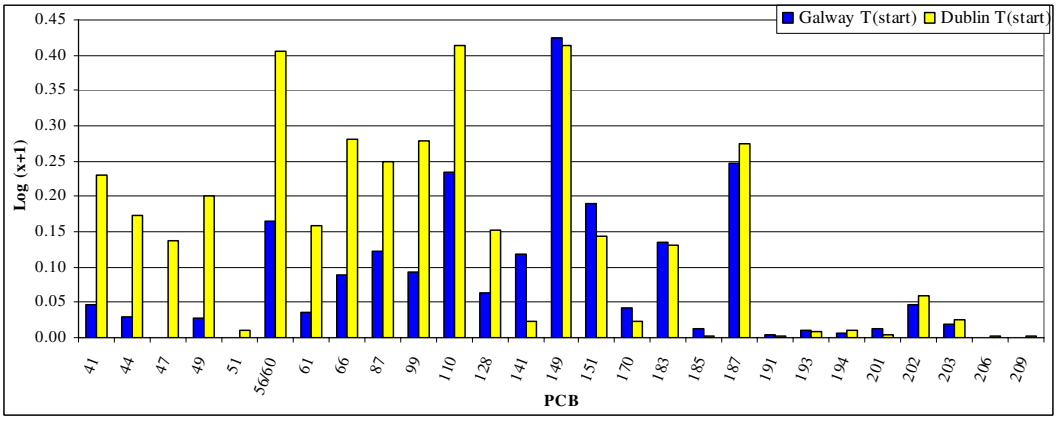

Figure 4.6: PCB concentrations (µg/kg dry weight) (Log(x+1)) in T(start) mussel samples taken from both the Galway and Dublin sites.

Overall PCB concentrations at the beginning and the end of the 6 week deployment period are comparable at the Dublin site, with the majority of PCB compounds having slightly increased in concentration (*Fig. 4.7*). PCBs 18, 31, 33, 74, 129 and 208 were not detected in the Dublin T(end) mussel sample.

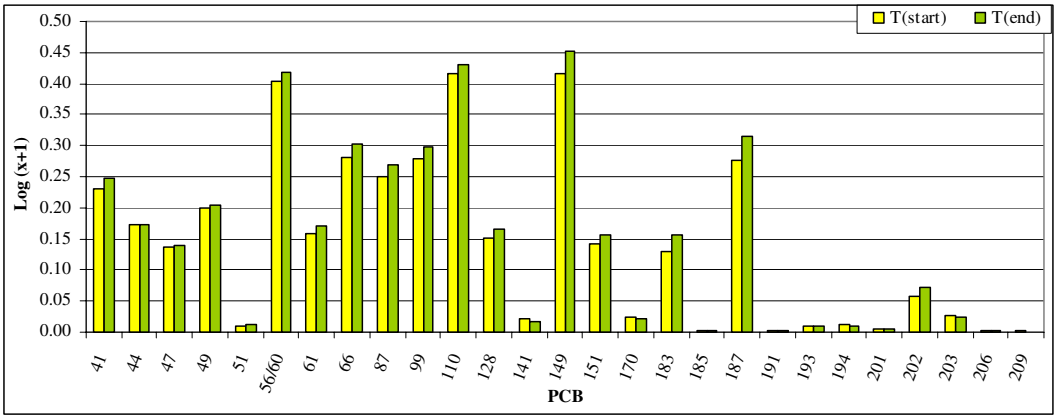

Figure 4.7: PCB concentrations (µg/kg dry weight) (Log(x+1)) in T(start) and T(end) mussel samples taken from the Dublin site.

The lipid content of the Native NBL mussel sample (2.02 %) is almost twice that of the Dublin T(end) sample (1.21 %), which may help to explain why the majority of the PCBs measured in NBL mussels are in excess of twice the levels detected in the Dublin T(end) sample (*Fig. 4.8*). As stated previously, the greater the lipid content of the aquatic organism, the greater the bioconcentration potential of the chemical [17]. Two PCBs (PCB 74 and PCB 209) were not detected in the Native NBL mussel sample.

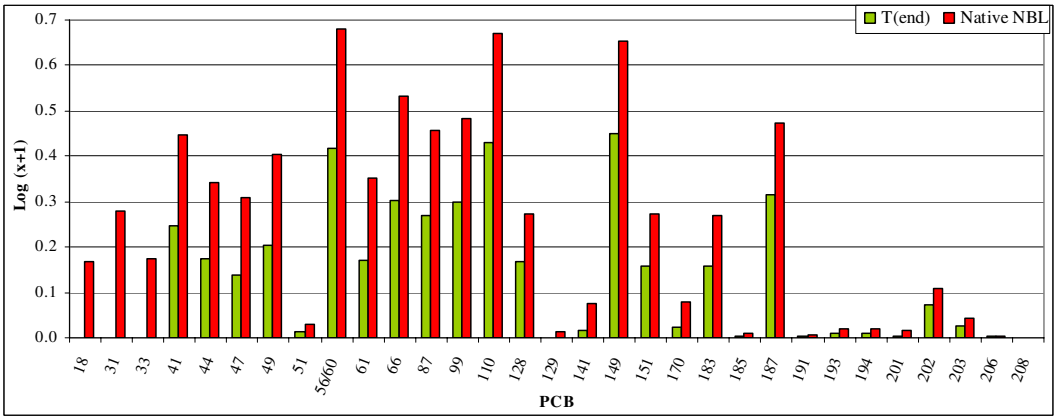

Figure 4.8: PCB concentrations (µg/kg dry weight) (Log(x+1)) in the T(end) mussel sample and a native/wild mussel from the Dublin site.

The relative PCB levels in an organism will change after uptake by them due to metabolic processes. Thus PCB congeners that are resistant to metabolism may be accumulated to a greater extent than more readily metabolized congeners [18]. While Safe [19] has provided a comprehensive review on PCB metabolism, James [20] has reviewed selected aspects of this topic.

Borlakoglu and Wilkins [21], Niimi and Oliver [22], and Andersson et al [23] have postulated some general rules concerning the structure of persistent and bioaccumulating PCBs. For instance, high degrees of chlorination in the biphenyl rings and a lack of vicinal hydrogen atoms usually favour enrichment in biota, while PCBs with vicinal hydrogen atoms, especially in *meta*- and *para*-positions, are more easily metabolized by cytochrome P-450 enzymes. The cytochrome P-450 enzyme capacity and selectivity differs from species to species, resulting in species-specific PCB patterns.

While most of the less chlorinated PCB congeners (tri- and tetrachlorobiphenyls) and some of the more highly chlorinated PCBs can be metabolised by fish, in general they do not metabolise organochlorines extensively [24]. As regards bivalves, they exhibit low or undetectable activity of enzyme systems that metabolise PAH and PCB, thus allowing the unmetabolised contaminants to be detected in the bivalves' tissues [16] i.e. PCBs are only slowly metabolized by mussels [25].

The three completely non-*ortho*-substituted PCB congeners (PCB 77, 126, 169) are members of the WHO PCBs. These three coplanar PCBs have demonstrated acute toxicity similar to that observed for 2,3,7,8-tetrachlorodibenzo*p*- dioxin and 2,3,7,8-tetrachlorodibenzofuran [26, 27], while Safe [28,29] has documented chronic toxicity effects.

Exposure of mussels to sediment-associated contaminants depends on water turbidity, feeding modes and on the location of the mussel in the water column [30]. Several studies have demonstrated that the accumulation of HOCs in aquatic organisms is influenced by changes in both the amount of dissolved and particulate organic matter (POM) in the water [31–34], with the partitioning of HOCs between water and particulate organic matter been shown to reduce the bioavailability of HOCs to gill-breathing organisms because of the decrease in the amount of freely dissolved contaminants available for uptake across the gill membranes.

Particle sorption is not likely however to reduce the bioavailability of HOCs to filter-feeding organisms [35, 36], such as *Mytilus edulis*, which consume suspended POM. Instead, in areas densely populated by blue mussels, filter feeding is a major mechanism of removal of suspended POM from the water column [37], and the high filtration capacity of the mussels indicates that HOCs associated to food particles is an important source of contaminant exposure [38]. Mussels accumulate contaminants from the dissolved, colloidal, and fine particulate phases [15].

In this present study, contaminants circulating in the top 1.5-2m of the water column would have been bioavailable to the mussels contained in the cages at the base of the passive sampling frames, (considering of course that the contaminants were in water soluble form or associated with suspended particulates and colloids).

4.5.2 Assessment of PCBs in the Spot Water Samples

As previously mentioned, all PCB concentrations fell below the LoQ values in the Dublin spot water sample. Thus an assessment of PCB levels was only possible in the Galway spot water sample. The concentration data graphically presented herein are taken from *Table 4.13* and *Table 4.14*.

4.5.2.1 Assessment of WHO and Marker PCBs in the Galway Spot Water Sample

WHO and Marker PCBs in the Galway spot sample are presented on a single graph (*Fig. 4.9*). PCB 118 appears twice, keeping in line with its presence as both a WHO and Marker PCB. WHO PCBs 114, 157 and 189 were not detected in the Galway spot water sample. Marker PCB 52 was also not detected. The most prevalent WHO PCBs are PCB 118 (202 pg/l) and PCB 77 (44.3 pg/l), while the most abundant Marker PCBs are PCB 28 (646 pg/l), PCB 138 (432 pg/l) and PCB 153 (420 pg/l).

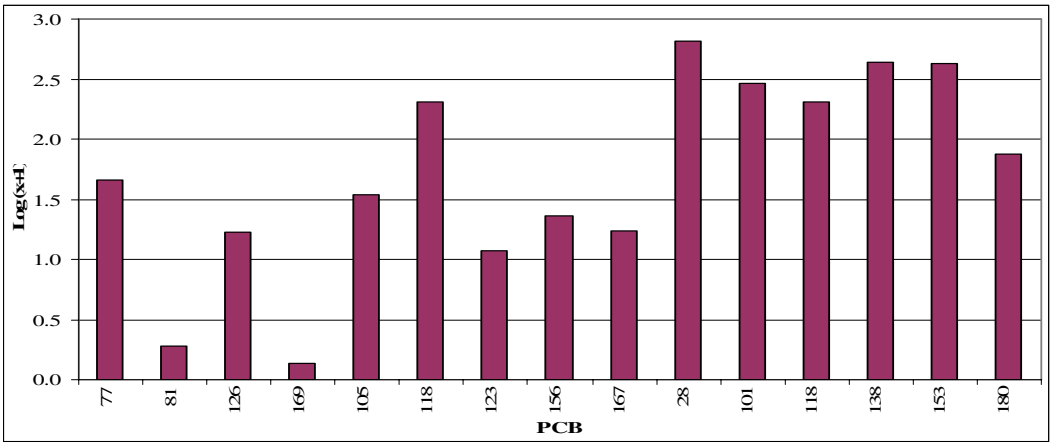

Figure 4.9: Concentrations of the WHO and Marker PCBs (pg/l) (Log(x+1)) detected in the Galway Spot water sample.

4.5.2.2 Assessment of "Other" PCBs in the Galway Spot Water Sample

Fig. 4.10 presents results of 16 PCBs in the Galway water sample. A total of 17 PCB compounds in this "other" grouping were below the limit of Quantification (LoQ), the values for which are included in *Table 4.14*. PCB 33 (431 pg/l) and PCB 31 (415 pg/l) were found in the highest concentrations in the Galway spot water sample, with PCBs 18, PCB 56/60, PCB 110 and PCB 149 just under half the concentration reported for PCB 33 (178-213 pg/l). The concentrations of the remaining 10 PCB compounds fall below 100 pg/l.

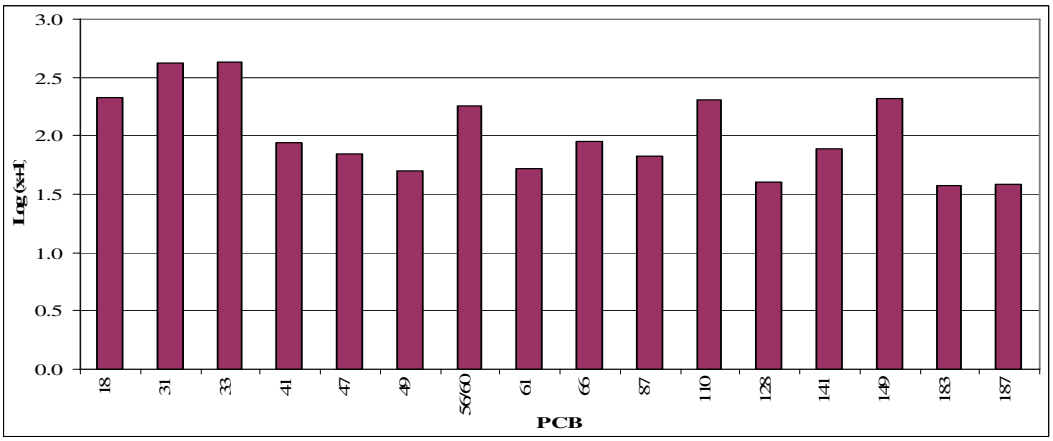

Figure 4.10: Concentrations of the Other PCBs (pg/l) (Log(x+1)) detected in the Galway Spot water sample.

Overall PCB concentrations in the Galway Spot water sample were low, (considering that 21 compounds were not detected below their LoQ) with the majority of those determined having concentrations <100 pg/l. It is not surprising that the marker PCBs have some of the most elevated concentrations reported, given that their classification is based on the fact that they are present in relatively high concentrations in technical mixtures [39].

Marker PCB 28 has the maximum concentration (646 pg/l) reported for all PCBs in the spot water sample. This is to be expected as it is one of the most water soluble PCBs (Log K_{ow}: 5.67 [40]). As regards the elevated levels (>400 pg/l) of the marker

hexacholorobiphenyl compounds (PCB 138 and PCB 153), their presence may indicate the importance of the particulate matter captured in the spot water sample. The relatively low solubility of these PCBs in water (Log K_{ow}: 6.83 and 6.92 [40]) may indicate that such compounds may partially be absorbed on the suspended solids and were extracted during the analysis.

PCB 33 and PCB 31 also have concentrations greater than 400 pg/l, having low octanol-water partition co-efficients (5.6 and 5.67 [40]) similar to PCB 28.

The analysis of the unfiltered spot water sample provides an insight into the contaminant phases present in the water column. These different phases are important with regard to the bioconcentration and bioaccumulation of contaminants by aquatic organisms i.e. dissolved aqueous contaminants can be absorbed by fish via the gills and body surface, while contaminants associated with particulate matter can be taken in via ingestion of food or through contaminated sediment.

4.5.3 Assessment of PS derived PCB Water Concentrations

The PS derived water concentrations discussed herein were determined using a combination of both literature and estimated Log $K_{sr,w}$ values. *Table 4.13* and *Table 4.14* document the concentration data used to derive the graphical outputs reported below.

4.5.3.1 PS derived WHO PCB Water Concentrations

While analysis of 12 WHO PCBs was completed, 3 were not detected in the PS membranes from both sites, (PCB 114, PCB 157 and PCB 189). All 9 remaining WHO

PCBs were detected in the Dublin sample, while only 6 of the 9 were detected in the Galway PS (See *Fig. 4.11*). The concentrations determined at the Dublin site are consistently higher than those at the Galway site, which may primarily be as a consequence of the greater industrial nature of the Dublin Bay test site. PCB 105 and PCB 118 were found to be the most dominant at both sites. Given that PCB 118 is also a member of the marker PCBs (due to its relatively high concentration in technical mixtures), it comes as no surprise that it is the most abundant WHO PCB.

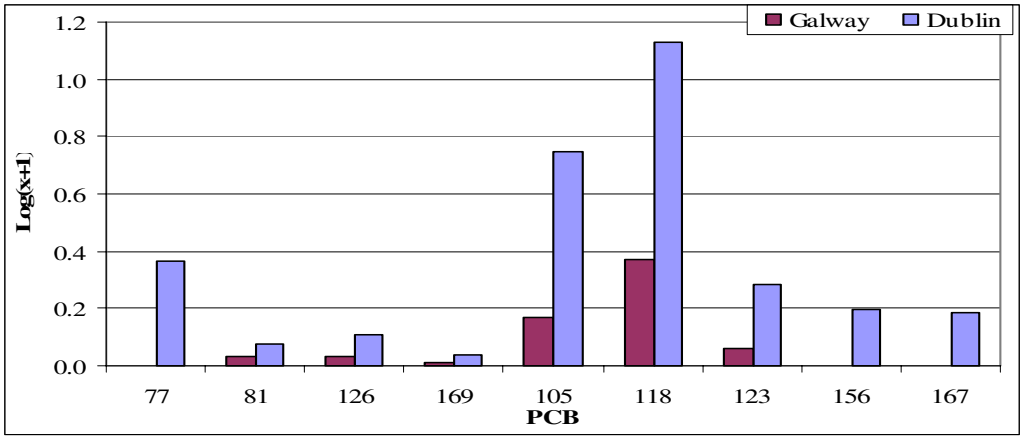

Figure 4.11: PS derived WHO PCB water concentrations (pg/l) (Log(x+1)) in Galway and Dublin as determined using a combination of literature (where available) and estimated Log $K_{sr,w}$ values.

4.5.3.2 PS derived Marker PCB Concentrations

All seven marker PCBs were detected in the PS membranes from both sample sites, with concentrations reported in the Dublin sample being consistently higher than those in the Galway sample (See *Fig. 4.12*). Dissolved levels of the lower chlorinated compounds are more prevalent, with PCB 28 (trichlorobiphenyl) and PCB 52 (tetrachlorobiphenyl) found to be the most elevated at both sites. The dissolved concentration levels generally appear to decrease in order of increasing degree of chlorination.

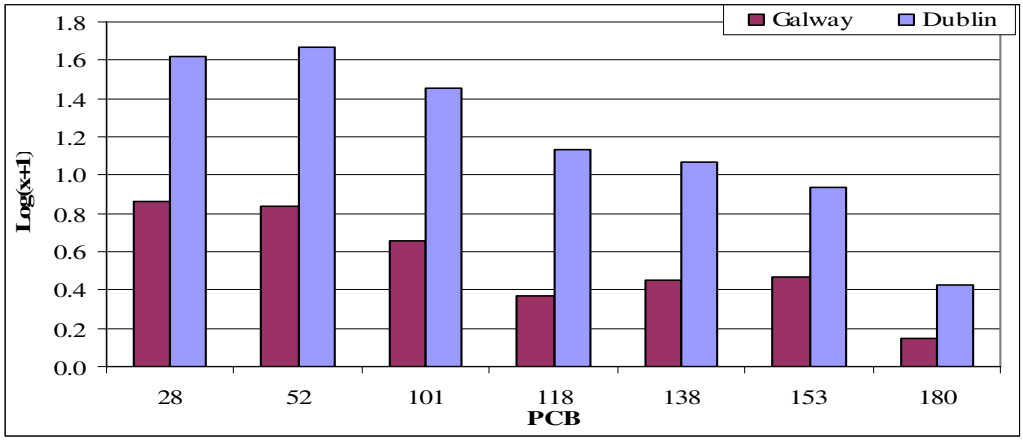

Figure 4.12: PS derived Marker PCB water concentrations (pg/l) (Log(x+1)) in Galway and Dublin as determined using a combination of literature (where available) and estimated Log $K_{sr,w}$ values.

4.5.3.3 PS derived Water Concentrations for "other" PCBs

A large number of PCB compounds in this category were not detected in the PS membranes from either site, including: PCB 74, 129, 141, 170, 183, 185, 191, 193, 194, 201, 202, 203, 206 and 208, with PCB128 not detected in the Galway PS. In line with other PCB groupings, levels of these PCBs were greater at the Dublin site compared to the Galway test site (See *Fig. 4.13*). In general, the dissolved water concentration of congeners decreased with increasing degree of chlorination. The overall congener profile is similar at both sites.

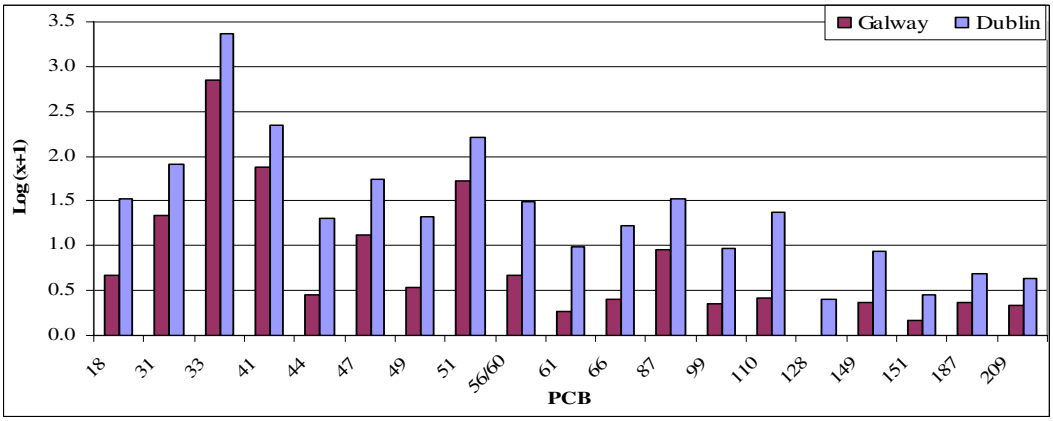

Figure 4.13: PS derived "other" PCB water concentrations (pg/l) (Log (x+1)) in Galway and Dublin as determined using a combination of literature (where available) and estimated Log $K_{sr,w}$ values.

4.6 Assessment of PAH Concentrations in Various Media

Section 4.6.1 details the PAH concentrations as detected in the test mussel tissues, expressed on both a dry weight basis and a lipid normalised dry weight basis (µg/kg) (See *Table 4.17*), while also investigating the use of PAH ratio information from the mussel tissue concentrations as an identification aid for determining PAH sources.

The dissolved PAH water concentrations (ng/l) (See *Table 4.15*), as determined from the various matrices, are assessed as follows:

4.6.1. Assessment of PAH in the Spot Water Samples

4.6.2 PS derived PAH Water Concentrations

4.6.1 Assessment of PAH Concentrations in Study Mussels

PAH concentrations in test mussels are reported in *Table 4.17*. An assessment of the concentrations of PAHs (Section 4.6.1.1) in addition to an investigation into PAH ratio information (Section 4.6.1.2) is discussed below.

Table 4.17: PAH concentrations µg/kg dry weight and in parenthesis (µg/kg dry weight and lipid normalised) in test site mussel samples

	Sample Type	Mussel (ug/kg)				
	Location	Galway		Dublin		
		T(start)	T(end)	T(start)	T(end)	Native NBL
US EPA PAHs	Naphthalene (N)	<4.55 (<3.50)	<4.90 (<3.50)	5.27 (4.39)	<4.50 (<3.72)	13.4 (6.63)
	Acenaphthylene (Acy)	<1.52 (<1.17)	<0.38 (<0.27)	2.70 (2.25)	2.17 (1.79)	2.76 (1.37)
	Acenaphthene (Ace)	<3.04 (<2.34)	<0.54 (<0.39)	0.95 (0.79)	<1.50 (<1.24)	1.64 (0.81)
	Fluorene (F)	1.35 (1.04)	0.69 (0.49)	3.30 (2.75)	4.54 (3.75)	5.48 (2.71)
	Phenanthrene (P)	15.6 (12.0)	14.3 (10.2)	31.6 (26.3)	38.2 (31.6)	59.9 (29.7)
	Anthracene (A)	1.15 (0.89)	1.84 (1.32)	5.39 (4.49)	10.1 (8.35)	9.32 (4.62)
	Fluoranthene (Fl)	11.0 (8.50)	15.2 (10.9)	40.1 (33.4)	39.6 (32.8)	77.2 (38.2)
	Pyrene (Py)	10.1 (7.77)	15.7 (11.2)	59.4 (49.5)	70.6 (58.4)	148 (73.5)
	Benzo[a]anthracene (BaA)	2.96 (2.28)	3.59 (2.57)	17.6 (14.6)	23.8 (19.7)	32.2 (15.9)
	Chrysene - Triphenylene (C-T)	5.83 (4.49)	7.73 (5.52)	36.1 (30.1)	54.4 (45.0)	81.4 (40.3)
	Benzo[b+j+k]fluoranthene (BbjkF)	7.45 (5.73)	9.79 (6.99)	52.1 (43.4)	74.9 (61.9)	50.8 (25.2)
	Benzo[a]pyrene (BaP)	1.33 (1.02)	1.89 (1.35)	11.8 (9.81)	19.5 (16.1)	22.2 (11.0)
	Indeno[1,2,3-cd]pyrene (IP)	1.45 (1.12)	1.56 (1.11)	8.38 (6.98)	9.97 (8.24)	8.25 (4.08)
	Benzo[ghi]perylene (BghiP)	1.79 (1.37)	2.44 (1.75)	12.3 (10.29)	13.9 (11.45)	11.3 (5.62)
	Dibenz[ah]anthracene (DahA)	<0.35 (<0.27)	0.56 (0.40)	2.37 (1.97)	2.80 (2.32)	3.53 (1.75)
Other PAHs	Benzo[b]naphtho [2,1-d] thiophene (BbN)	0.93 (0.71)	1.31 (0.93)	10.2 (8.51)	13.9 (11.5)	25.5 (12.6)
	Benzo[c]phenanthrene (BcP)	1.81 (1.39)	2.66 (1.90)	5.45 (4.54)	9.31 (7.69)	7.03 (3.48)
	Benzo[ghi]fluoranthene (BghiF)	1.99 (1.53)	2.86 (2.05)	10.1 (8.42)	14.9 (12.3)	8.62 (4.27)
	Benzo[e]pyrene (BeP)	5.98 (4.60)	9.44 (6.74)	42.1 (35.0)	75.4 (62.3)	50.9 (25.2)
	Anthanthrene (An)	<0.51 (<0.39)	<0.54 (<0.39)	1.35 (1.12)	2.57 (2.12)	<3.18 (<1.58)
	Coronene (Co)	0.57 (0.44)	0.62 (<0.44)	3.03 (2.52)	1.29 (1.07)	<1.82 (<0.90)
PAH Ratios	P/A	13.6 (13.5)	7.77 (7.73)	5.86 (5.86)	3.78 (3.78)	6.43 (6.43)
	Fl/Py	1.09 (1.09)	0.97 (0.97)	0.68 (0.67)	0.56 (0.56)	0.52 (0.52)
	A/178	0.07 (0.07)	0.11 (0.11)	0.15 (0.15)	0.21 (0.21)	0.13 (0.13)
	BaA/228	0.34 (0.34)	0.32 (0.32)	0.33 (0.33)	0.30 (0.30)	0.28 (0.28)
	Fl/(Fl+Py)	0.52 (0.52)	0.49 (0.49)	0.40 (0.40)	0.36 (0.36)	0.34 (0.34)
	IP/(IP+BghiP)	0.45 (0.45)	0.39 (0.39)	0.41 (0.40)	0.42 (0.42)	0.42 (0.42)

PAH ratios as follows: P/A: phenanthrene/anthracene; Fl/Py: fluoranthene/pyrene; A/178: anthracene/anthracene + phenanthrene; BaA/228: benzo[a]anthracene/benzo[a]anthracene + chrysene; Fl/Fl + Py: fluoranthene/fluoranthene + pyrene; IP/IP + BghiP: indeno[1,2,3-c,d]pyrene/indeno[1,2,3-c,d]pyrene + benzo[g,h,i]perylene. The PAH ratios dicussed in below relate to those determined from the PAH concentrations detemined on a dry weight basis (µg/kg dry wgt).

4.6.1.1 Assessment of PAHs in Test Mussels

Although the PAH results presented in *Table 4.17* above have been divided into the "US EPA PAHs" and "other PAHs", all PAHs (n=21) are included on single graphs for each discussion section herein. In the case where a compound was not detected (i.e. the concentration fell below the LoQ), the relevant LoQs are reported in *Table 4.17* but the compounds were omitted from the graphical representation of results.

4.6.1.1.1 Assessment of PAHs in Galway Mussels

A number of PAH compounds were not detected in the Galway mussels i.e. naphthalene, acenaphthylene, acenaphthene and anthanthrene, with dibenzo[a,h]anthracene not detected in the T(start) mussels. Mussels at the Galway site were found to be more enriched in the low molecular weight PAHs, namely phenanthrene, fluoranthene, pyrene, chrysene-triphenylene, benzo[b+j+k]fluoranthene and benzo[e]pyrene relative to the higher molecular weight PAHs., thus indicating the accumulation of more water soluble PAHs at this site. With two exceptions (i.e. fluorene (1.35 Vs 0.69 µg/kg dry weight) and phenanthrene (15.6 Vs 14.3 µg/kg dry weight)), PAH concentrations in the Galway mussels were greater in the T(end) sample than the T(start) mussels, indicating that bioaccumulation occurred during the deployment period (See *Fig. 4.14*). It should be noted that total lipid levels are similar for these samples.

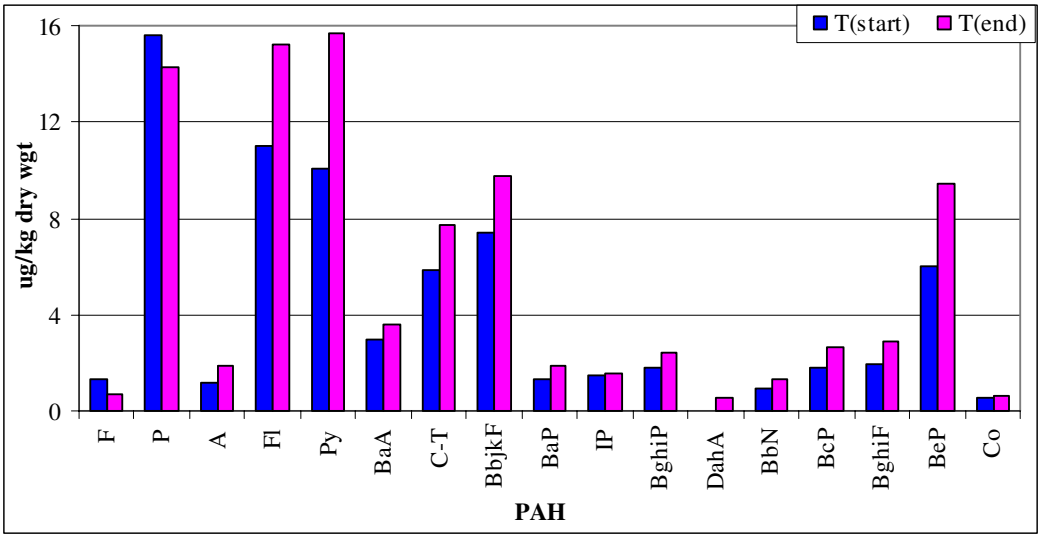

Figure 4.14: PAH concentrations (µg/kg dry wgt) in T(start) and T(end) mussels from the Galway site.

4.6.1.1.2 Assessment of PAHs in Dublin Mussels

The PAH concentrations of the Galway T(start) and Dublin T(start) mussel samples are presented in *Fig. 4.15* below. The Galway T(start) concentrations represent the initial level of PAH in the mussels used for the PSTS at the Dublin location. The Dublin T(start) mussels are thus representative of the 26 day equilibration period at the NBL prior to the PS deployment.

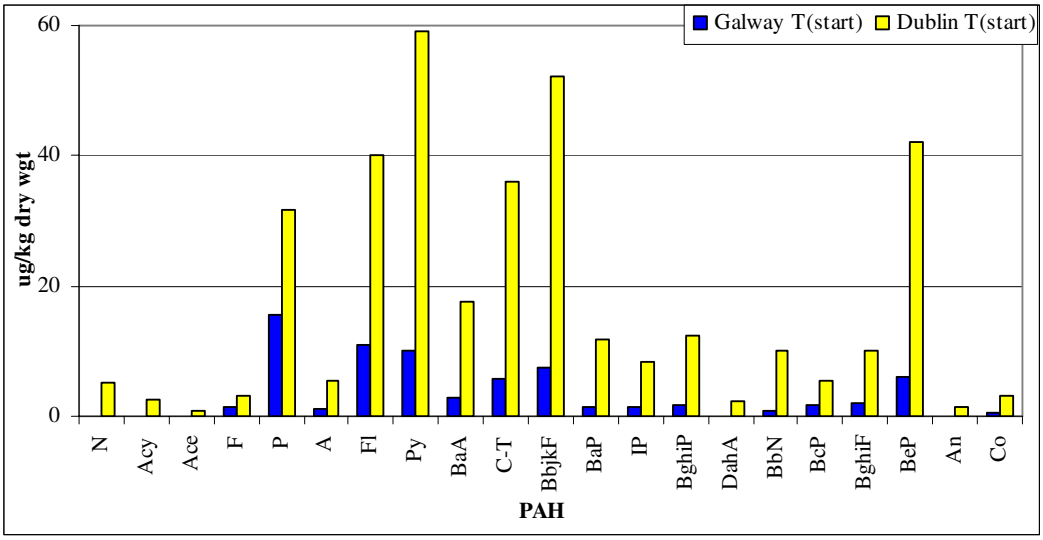

Figure 4.15: PAH concentrations (µg/kg dry wgt) in T(start) mussel samples taken from both Galway and Dublin sites.

Mussels transferred from the T(start) site at Galway (naphthalene, acenaphthylene, acenaphthene, dibenzo[a,h]anthracene and anthanthrene not detected) to the Northbank lighthouse rapidly accumulated PAH during the 26 days of equilibration, demonstrating that the PAH in Dublin Bay were bioavailable. Following the 26 day equilibration period at the Northbank Lighthouse, mussel's bioaccumulated a variety of PAH compounds (e.g. pyrene, benzo[b+j+k]fluoranthene, benzo[e]pyrene, fluoranthene, chrysene-triphenylene and phenanthrene). Having equilibrated in an extensively used shipping lane, the accumulation of the tetra aromatics (from petroleum) is evident.

Exposure to contaminants from different environmental compartments will ultimately result in different organism contaminant residues. In low turbidity water, filter-feeding organisms are mainly exposed to the dissolved fraction of the hydrophobic contaminants [41], and this is evident as discussed for the Galway mussels (suspended solids 5 mg/l (*Table 4.3*)). Increases in water turbidity, such as that experienced by the equilibrating mussels (suspended solids 20.6 mg/l (*Table 4.3*)) can influence bioaccumulation of contaminants adsorbed on sediment grains [41, 42]. Thus, in turbid areas where mussels are mainly exposed to particulate contamination, the higher molecular weight compounds (pent and hexa- aromatics) can accumulate to a greater extent. Potential influences (e.g. resuspension of sediments) may result in the greater accumulation of higher molecular weight compounds (as evidenced in Dublin Bay samples) as a consequence of the ingestion of sediment associated compounds.

With three exceptions (naphthalene (5.27 Vs <4.5 µg/kg dry weight), acenaphthylene (2.70 Vs 2.17 µg/kg dry weight) and coronene (3.03 Vs 1.29 µg/kg dry weight), PAH concentrations in the equilibrated mussels were greater at the end of the 6 week exposure study than at the start, indicating that bioaccumulation of PAH occurred during the exposure period (*Fig. 4.16*).

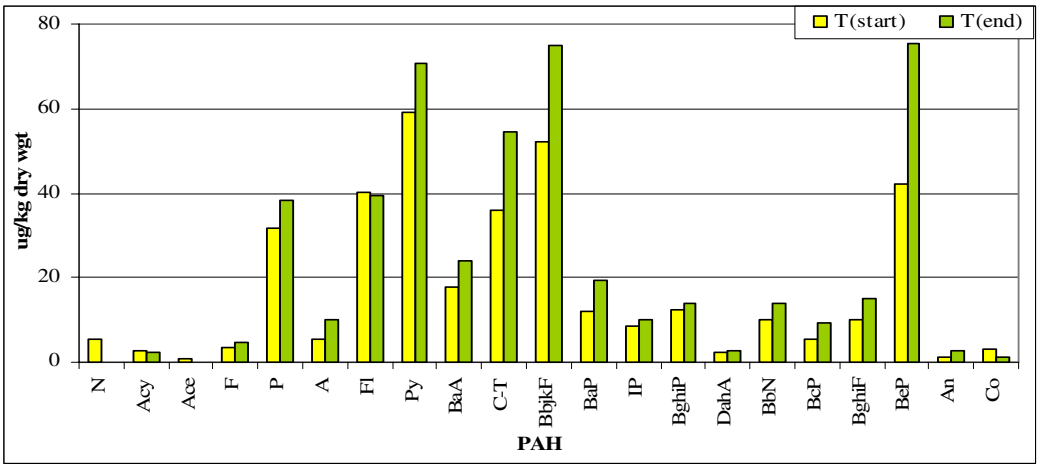

Figure 4.16: PAH concentrations (µg/kg dry wgt) in T(start) and T(end) mussel samples taken from the Dublin site.

Fig. 4.17 compares PAH concentrations detected in the T(end) Dublin mussel to those of the native mussel sample from the Northbank Lighthouse. The lower molecular weight PAHs are more abundant in the Native NBL sample (exception anthracene), while the higher molecular weight PAHs are generally present at greater concentrations in the T(end) sample (exceptions: benzo[a]pyrene, dibenzo[ah]anthracene, benzo[b]naphtha[2,1-d]thiophene and possibly anthanthrene (T(end): 2.57 µg/kg dry weight Vs LoQ of Native NBL: 3.18 µg/kg dry weight) and coronene (T(end): 1.29 µg/kg dry weight Vs LoQ of Native NBL: 1.82 µg/kg dry weight)).

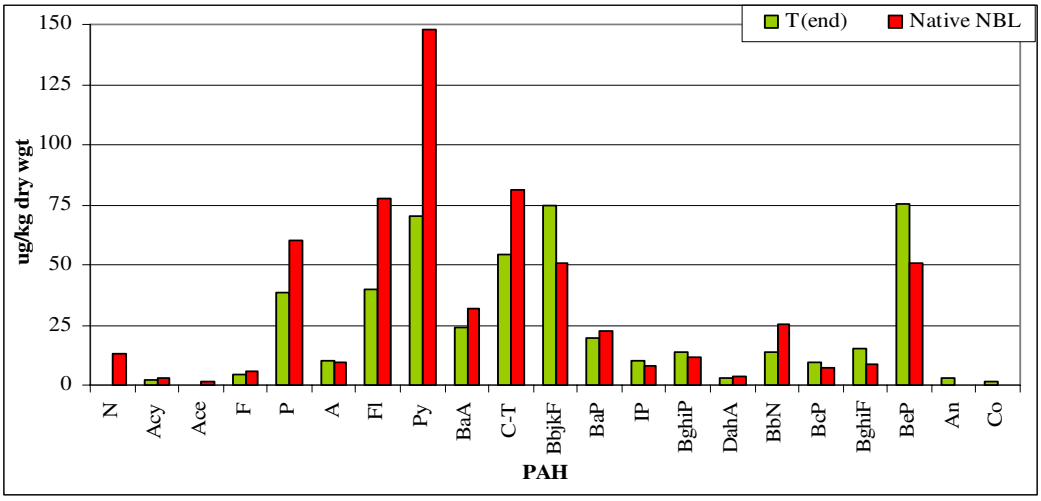

Figure 4.17: PAH concentrations (µg/kg dry wgt) in the T(end) mussel sample and a native wild mussel sample (Native NBL) taken from the Dublin site.

In general the most abundant PAH in the mussel samples were found to be pyrene, fluoranthene, phenanthrene, chrysene-triphenylene, benzo[b+j+k]fluoranthene and benzo[e]pyrene. Concentrations of PAH in mussel tissues reflect the time integrated concentrations of bioavailable PAH in the ambient water. They include the water-soluble fraction and particles (sediment and food), as well as unassimilated PAH associated with particles on the gills or in the gut [(43)]. PAH associated with particulate matter are generally less bioavailable to mussels than dissolved PAH [(43)].

However, Axelman et al [44] observed that mussels in the field bioconcentrate higher tissue concentrations of PAH from the particulate phase than the dissolved phase when the concentration of PAH associated with suspended small particles (>0.7 μm) and colloidal organic matter is greater than that of dissolved PAH.

Water solubility governs the tri-aromatic isomer distribution i.e. phenanthrene and anthracene. Given that phenanthrene is about 20 times more water soluble than anthracene [45], the resulting P/A values are usually high. The use of such ratios is further described below.

In many studies, benzo[a]pyrene has been shown to be carcinogenic in contrast to its structural isomer benzo[e]pyrene [46]. Therefore, the difference of concentration of the two isomers in the mussel tissues examined may be related to the greater carcinogenicity of benzo[a]pyrene resulting in its preferential biotransformation while benzo[e]pyrene was preferentially accumulated in the lipids [47].

In order to further investigate this, the benzo[a]pyrene (BaP): benzo[e]pyrene (BeP) ratio in the Spot water samples (dissolved and particulate phase) and the PS derived water concentrations (dissolved phase only) were compared to those in the various mussel samples (See *Fig. 4.18(a)*). The ratios observed in the caged study mussel samples (0.20-0.28) and the Native NBL mussels (0.44) are much lower than those in the other two matrices (Spot: 0.68-1.17 and PS: 0.73-0.88). This suggests a capacity within mussels to preferentially reduce their BaP burden and/or convert BaP to the less toxic BeP, as suggested by Baumard et al [47]. Such an observation has consequences in terms of where only mussels are utilised to carry out environmental monitoring of BaP.

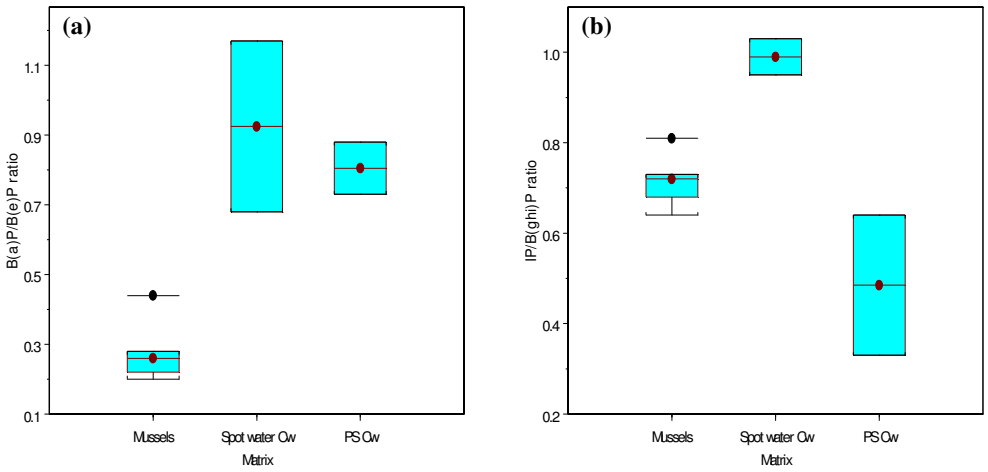

Figure 4.18: (a) Benzo[a]pyrene (BaP): benzo[e]pyrene (BeP) ratios and (b) Indeno[1,2,3-cd]pyrene (IP): benzo[ghi]perylene (BghiP) ratios for mussel, spot water and PS samples.

Indeno[1,2,3-cd]pyrene is less abundant in all mussel samples than benzo[ghi]perylene. According to Baumard et al [47] the difference observed in the levels of these isomers could be attributed to a partial biotransformation of indeno[1,2,3-cd]pyrene (See *Fig. 4.18(b)*). Although the indeno[1,2,3-cd]pyrene (IP): benzo[ghi]perylene (BghiP) ratio for the PS membranes (0.33-0.64) is lower than that for the mussels (0.64-0.81), the differences are not as definitive as for the BaP:BeP data. Further side-by-side deployment of PS and mussels would be required to make a more definitive conclusion.

The filtering behaviour of mussels can have a profound effect on contaminant uptake. A higher filtering rate induces a greater exposure to the contaminants present in the water column. *Mytilus edulis* feeding/filtering rates in November and December are generally lower due to limited availability of food and lower water temperatures (8.65 ^{o}C in Galway and 8.26 ^{o}C in Dublin (*Table 4.3*)). Bivalves have been observed to display a yearly cycle in the uptake of contaminants, due to changes associated with their reproductive cycle and lipid content [47-49]. However, as this study was only completed during the months of November and December, the potential influence of such temporal effects could not be further investigated.

Experimental and field studies have demonstrated that it takes 2-3 months to reach equilibrium between PAH concentrations in mussels and the environment [50], this being in line with the exposure period of test mussels transplanted from the Galway to Dublin site (i.e. 26 day equilibration and 44 day deployment = 70 days) (See Section 4.7.2). The results of an experiment carried out by Peven et al [16] suggest that if mussels from similar regions are used, the transplanted mussels appear to attain concentrations of contaminants similar to those of native animals within 40–50 days.

4.6.1.2 Investigation into the use of PAH Ratios to describe Hydrocarbon Sources

The use of PAH ratio information has been well documented in order to further describe hydrocarbon sources. A number of such ratios (as introduced in *Table 2.1* and *Table 4.18*) are discussed below.

The PAH ratios, phenanthrene/anthracene (P/A) and fluoranthene/pyrene (Fl/Py,) were determined for each of the mussel samples and are shown in *Table 4.17*. The resultant values (on a dry weight basis) when plotted in *Fig. 4.19*, provide valuable information in relation to hydrocarbon sources being petrogenic or pyrogenic.

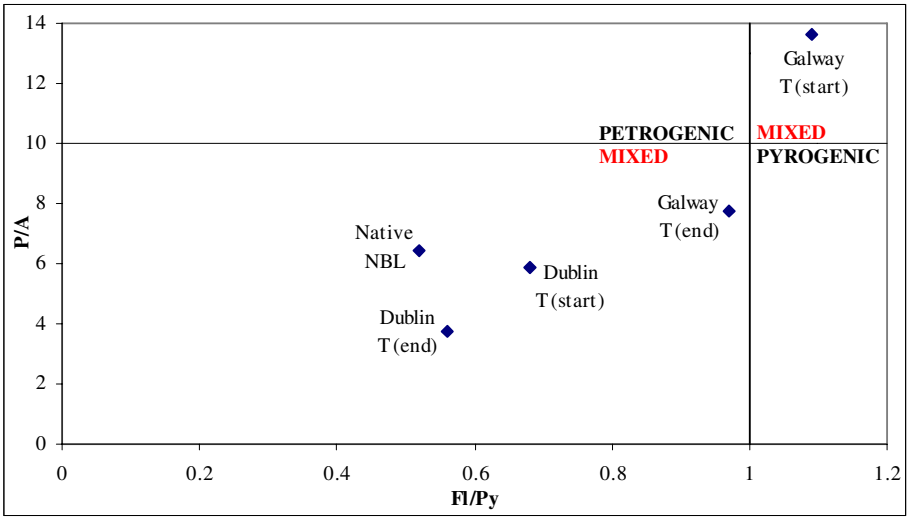

Figure 4.19: PAH concentration ratios (P/A: phenanthrene/anthracene; Fl/Py: fluoranthene/pyrene) as determined using the mussel tissue sample concentrations on a dry weight basis (µg/kg dry wgt).

Further PAH ratios namely: anthracene / (anthracene + phenanthrene) (A/178); benzo[a]anthracene/ (benzo[a]anthracene + chrysene) (BaA/228); fluoranthene / (fluoranthene + pyrene) (Fl/(Fl + Py)) and indeno[1,2,3-c,d]pyrene / (indeno[1,2,3-c,d]pyrene + benzo[g,h,i]perylene) (IP/(IP + BghiP)) were also determined (*Table 4.18*). The resulting ratio values are reported in *Table 4.17* and are discussed below.

Table 4.18: PAH isomer pair and "cut-off" ratios used in identification of PAH sources

Source	**PAH isomer ratios**			
	A/178	**BaA/228**	**Fl/(Fl+Py)**	**IP(IP+BghiP)**
Petroleum (unburned)	<0.10	<0.20	<0.40	<0.20
Petroleum combustion			0.40-0.50	0.20-0.50
Petroleum and combustion (mixed)		0.20-0.35		
Combustion	>0.10	>0.35		
Biomass and coal combustion			>0.50	>0.50

PAH isomer pair ratios Yunker et al [51], A/178: anthracene/(anthracene + phenanthrene), BaA/228: benzo[a]anthracene/(benzo[a]anthracene + chrysene), Fl/(Fl + Py): fluoranthene/(fluoranthene + pyrene), IP/(IP + BghiP): indeno[1,2,3-c,d]pyrene/(indeno[1,2,3-c,d]pyrene + benzo[g,h,i]perylene).

4.6.1.2.1 Assessment of PAH Ratios in Galway Mussels

The PAH ratios determined from the Galway T(start) and T(end) mussel samples indicate mixed sources of PAH at the Galway site, with Galway T(start) mussels having a P/A of 13.6 (>10) and a Fl/Py of 1.09 (>1) and the T(end) mussel sample having a P/A of 7.77 (<10) and a Fl/Py of 0.97 (<1). Both Galway samples thus appear in the mixed source section of *Fig. 4.19*.

The BaA/228 ratio in the T(start) mussel sample of 0.34 (0.20-0.35) indicates a mixed PAH source, from both petroleum and combustion. This is reiterated by an A/178 ratio of 0.07 (<0.10), indicating unburned petroleum and an IP/(IP + BghiP) ratio of 0.45 (0.20-0.50) which indicates petroleum combustion. The combustion source is supported by the Fl/(Fl + Py) ratio of 0.52 (>0.50), indicating biomass and coal combustion.

Similar to the T(start) mussel sample, the BaA/228 ratio in the T(end) mussel sample of 0.32 (0.20-0.35) indicates a mixed PAH source, from both petroleum and combustion. The remaining three ratios reinforce this finding, with a Fl/(Fl + Py) ratio of 0.49 (0.40-0.50) and an IP/(IP + BghiP) ratio of 0.39 (0.20-0.50) both indicating petroleum combustion, and the A/178 ratio of 0.11 (>0.10) indicating combustion sources.

4.6.1.2.2 Assessment of PAH Ratios in Dublin Mussels

The PAH ratios as determined from the Dublin T(start) and T(end) mussel samples also both indicate mixed sources of PAH, with a P/A of 5.86 and 3.78 (<10) and a Fl/Py of 0.68 and 0.56 (<1) respectively. In addition, the native NBL sample follows the same trend, with a P/A of 6.43 (<10) and a Fl/Py of 0.52 (<1). Thus, all three Dublin mussel samples appear in the mixed source section of *Fig. 4.19*.

The BaA/228 ratios determined in all three Dublin mussel samples (0.33; 0.30; 0.28) indicate mixed sources of PAH from petroleum and combustion (0.20-0.35). The A/178 ratios (0.15; 0.21; 0.13) support this, indicating combustion sources (>0.10), while the IP/(IP+BghiP) ratios (0.41; 0.42; 0.42) indicate petroleum combustion (0.20-0.50). The Fl/(Fl+Py) ratios differs slightly between the mussel samples. The ratio for Dublin T(start) i.e. 4.0 indicates a petroleum combustion source (0.40-0.50) while the ratios for Dublin T(end) and the Native NBL (0.36; 0.34) indicate unburned petroleum (<0.40).

It should be noted that definitive source identification is not possible from PAH ratios alone (especially close to “cut-off” values) and the potential for metabolic/excretion capabilities in addition to mixed source influences must additionally be addressed when completing such assessments.

4.6.2 Assessment of PAH in the Spot Water Samples

The PAH Spot water concentrations (See *Table 4.15*) for both locations are depicted in *Fig. 4.20* below.

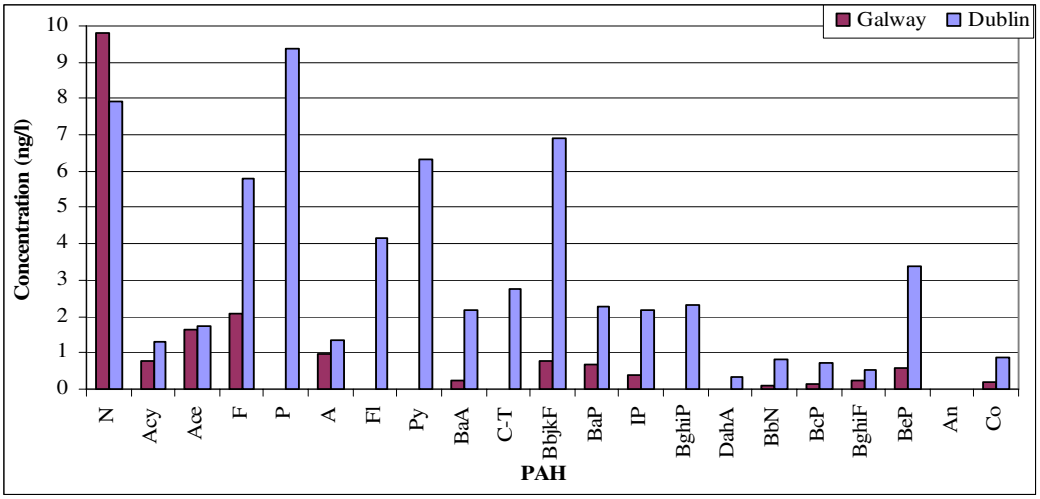

Figure 4.20: PAH concentrations (ng/l) in spot water samples from Galway and Dublin.

In general, the concentrations of each individual PAH measured in the spot samples are greater in Dublin than those in Galway, with the only exception being naphthalene (7.91 Vs 9.78 ng/l). In Dublin the profile was dominated by phenanthrene followed by naphthalene. Naphthalene is the most water soluble PAH (30.2 g/m^3 [(3)]), having a solubility approximately 7.5 times greater than acenaphthylene (3.93 g/m^3 [(3)]). Anthanthrene was not detected at either site, while phenanthrene, fluoranthene, pyrene, chrysene–triphenylene, benzo[g,h,i]perylene and dibenzo[ah]anthracene were not detected at the Galway site.

All 16 US EPA PAHs are represented in the Dublin spot water sample at concentrations of >1 ng/l, with the exception of dibenzo[ah]anthracene (0.35 ng/l). The increased level of suspended particulate matter in the Dublin water sample may partially account for the greater representation of the heavier molecular weight PAHs.

PAH solubility decreases as the octanol-water partition co-efficient (K_{ow}) and molecular weight increases, thus the lower molecular weight PAHs are preferentially dissolved in the water column while the heavier molecular weight compounds are preferentially absorbed onto and associated with particles.

Phenanthrene is approximately 20 times more soluble in water than anthracene [45]. These differences in solubility may partially explain the distribution of the isomer profile in the Dublin Spot sample. The PAH ratios as determined from the Dublin Spot sample indicate a mixed source of PAH with a P/A of 6.98 (<10) (pyrogenic) and a Fl/Py of 0.66 (<1) (petrogenic). No comparable ratios were available for the Galway spot sample, as 3 of the 4 isomers required were not detected in the water sample.

4.6.3 PS derived PAH Water Concentrations

With the exception of naphthalene, PS derived PAH C_w are consistently higher at the Dublin site than at Galway (See *Table 4.15* and *Fig. 4.21*). While the concentration of naphthalene (the most soluble PAH) was highest in Galway, the concentration of phenanthrene, which is approximately 20 times more soluble than anthracene, was found to be highest in Dublin. The PAH profile in the Dublin sample exhibited greater relative concentrations of higher condensed PAHs compared to Galway.

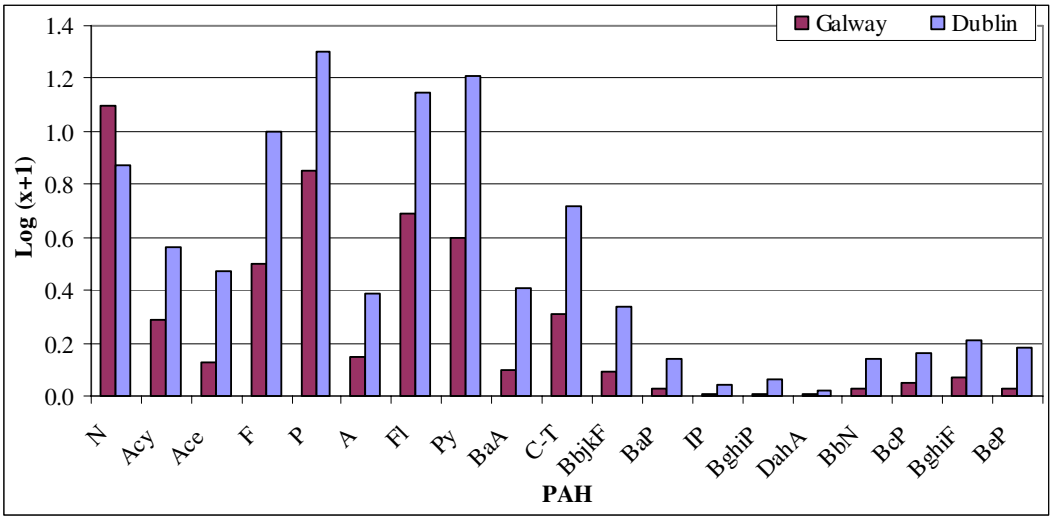

Figure 4.21: PS derived PAH water concentrations (ng/l) (Log (x+1)) in Galway and Dublin as determined using a combination of literature (where available) and estimated Log Ksr,w values.

4.6.3.2 PAH Ratios from PS derived C_w

The PAH ratios from *Table 4.15* are plotted in *Fig. 4.22* below. As described previously, the PS derived PAH concentrations have been determined using estimated and literature Log $K_{sr,w}$ values. Ratios determined from PAH concentrations using estimated Log $K_{sr,w}$ values are denoted by ^{Est} in this Section and in *Fig. 4.22*, while those ratios determined from PAH concentrations using literature Log $K_{sr,w}$ values are denoted by ^{Lit}.

The PAH ratios as determined from the Galway PS indicate a mixed source of PAH, with a P/A of 13.0 ^{Est}/15.0 ^{Lit} (>10) and a Fl/Py of 1.22 ^{Est}/1.32 ^{Lit} (>1). The PAH ratios as determined from the Dublin PS indicate a petrogenic source of PAH with a P/A of 12.4 ^{Est}/13.0 ^{Lit}/ (>10) and a Fl/Py of 0.85 ^{Est}/0.87 ^{Lit}/ (<1).

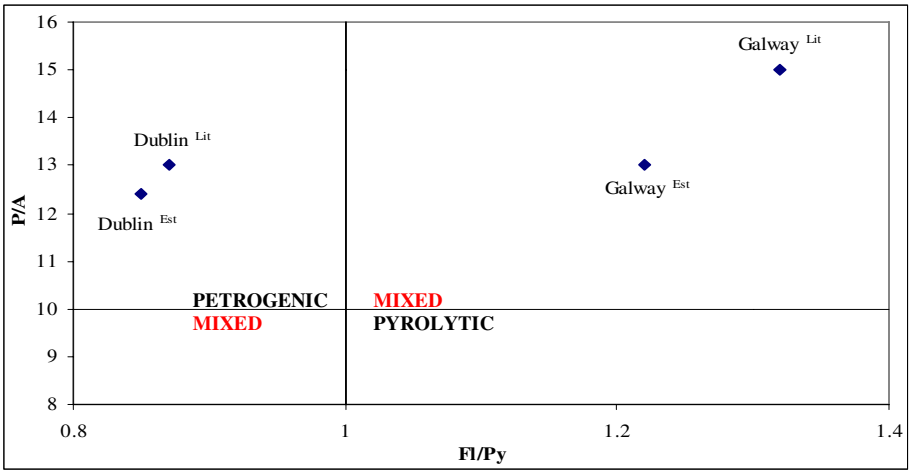

Figure 4.22: PAH concentration ratios (P/A: phenanthrene/anthracene; Fl/Py: fluoranthene/pyrene) as determined using the PS derived water concentrations (ng/l).

While the BaA/228 ratio from the Galway PS derived water concentrations of 0.19 ^{Est} (<0.20) and the A/178 ratio of 0.07 ^{Est}/0.06 ^{Lit} (<0.10) both indicate unburned petroleum, combustion sources have been identified through the IP/(IP + BghiP) ratio of 0.25 ^{Est}/0.25 ^{Lit} (0.20-0.50) indicating petroleum combustion and the Fl/(Fl + Py) ratio of 0.55 ^{Est}/0.57 ^{Lit} (>0.50) indicating biomass and coal combustion.

The BaA/228 ratio from the Dublin PS derived water concentrations of 0.27 ^{Est} (0.20-0.35) indicates a mixed source of petroleum and combustion. While the A/178 ratio of 0.07 ^{Est}/0.07 ^{Lit} (<0.10) indicates unburned petroleum, the remaining ratios reinforce the combustion source identified by the BaA/288 ratio. That is, the IP/(IP + BghiP) ratio of 0.39 ^{Est}/0.39 ^{Lit} (0.20-0.50) indicates petroleum combustion while the Fl/(Fl + Py) ratio of 0.46 ^{Est}/0.46 ^{Lit} (>0.50) indicates biomass and coal combustion.

4.7 Investigation into the Generation of Mussel Models

The following Section compares a selection of PCB and PAH Log BAF models generated during the course of this thesis with existing BCF models from literature, namely from work carried out by Geyer et al [17] and Thorsen et al [52]. Additionally, this Section also investigates the generation of an equilibrium model to determine whether the transplanted Galway mussels reached the same level of equilibrium as the Native NBL mussels during the 70 day deployment period in Dublin Bay. This Section is thus divided as follows:

4.7.1 Comparison of BAF models with existing models from literature.

4.7.2 Generation of Equilibration models.

4.7.1 Comparison of BAF Models with Existing Models from Literature

It should be noted that PCB and PAH models generated during this thesis utilised PS derived water concentrations and combined (estimated and literature) Log $K_{sr,w}$ values.

4.7.1.1 Geyer's Log BCF_L Model

According to Geyer et al [17], *Eqn. 1.4* (Section 1.3.1.1.3) can be used for the prediction of BCF_L values of relatively persistent organic chemical in mussels if their lipid content is known:

$$\text{Log } BCF_L = 0.956 \text{ Log } K_{ow} + 0.22 \qquad \textbf{\textit{Eqn. 1.4}}$$

In order to compare the PCB and PAH models described previously (determined using Log BCF values based on a wet weight basis) with *Eqn. 1.4*, they must be normalised to take account of the lipid content. The new (BAF) models are shown in *Fig. 4.23a* (n=6

PCBs), *Fig. 4.23b* (n=22 PCBs) and *Fig. 4.24* (n=16 PAH), whereby the Log BCF_L (Galway T(end), Dublin T(end) and Native NBL mussels) are plotted against the Log K_{ow} values. Only compounds for which BCF_L values were available for all samples of interest were included (i.e. n=6 for the Marker PCBs in *Fig. 4.23a* as no BCF_L was available for PCB 28 in the Dublin T(end) sample). BCF_L values for 16 PAH compounds were available, as are presented in *Fig. 4.24*.

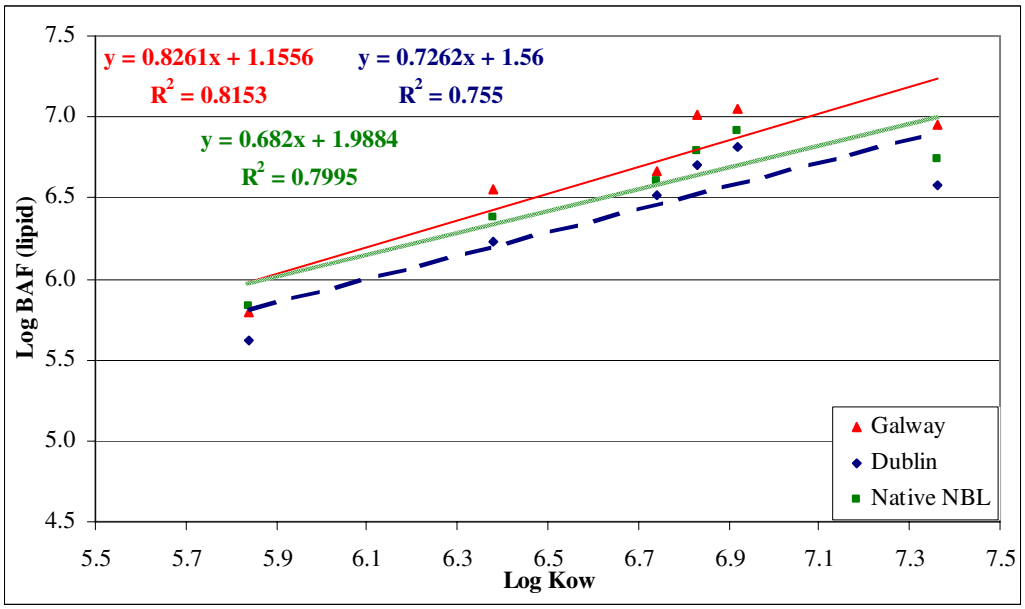

Figure 4.23a: Marker PCB (n=6) Log BAF_L plotted against the Log K_{ow} for Galway T(end), Dublin T(end) and Native NBL mussels (using PS derived C_w (combined Log $K_{sr,w}$ values)).

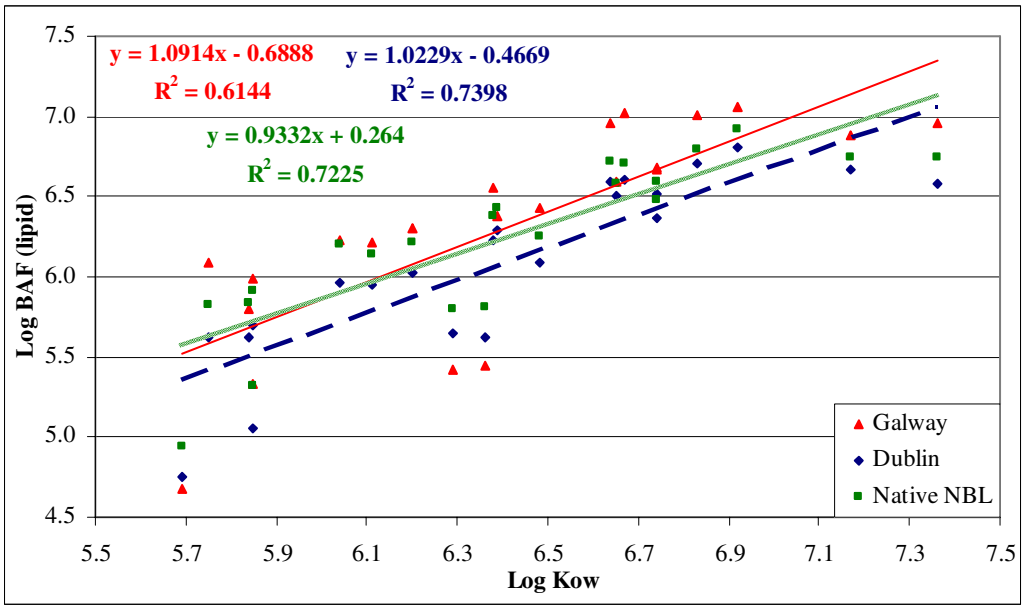

Figure 4.23b: PCB (n=22) Log BAF_L plotted against the Log K_{ow} for Galway T(end), Dublin T(end) and Native NBL mussels (using PS derived C_w (combined Log $K_{sr,w}$ values)).

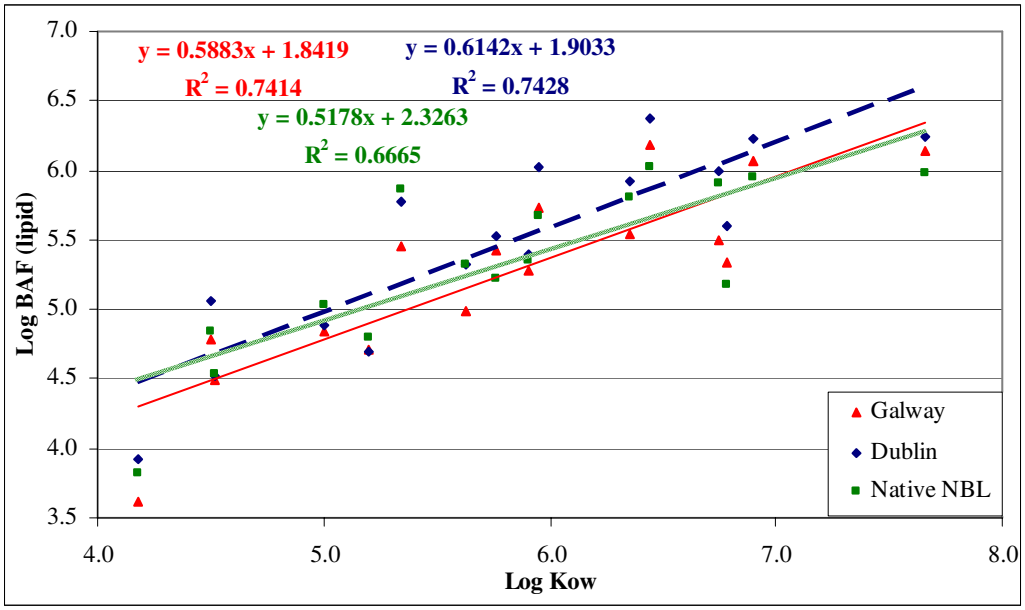

Figure 4.24: PAH (n=16) Log BAF_L plotted against the Log K_{ow} for Galway T(end), Dublin T(end) and Native NBL mussels (using PS derived C_w (combined Log $K_{sr,w}$ values)).

4.7.1.2 Thorsen's Log BCF Model (PAH)

A flow-through study carried out by Thorsen et al [52], measuring the uptake of PAHs by the freshwater mussel, *Elliptio complanata*, was conducted to determine bioconcentration factors (BCF) for 36 PAHs. A plot of Log BCF values versus Log K_{ow} for individual PAH analytes yielded the following steady-state bioconcentration regression equation:

$$\text{Log BCF} = 0.749\ (\text{Log } K_{ow}) - 1.060\ [R^2 = 0.8832] \qquad \textit{Eqn. 4.1}$$

The model generated by Geyer et al [17] is based on lipid (BCF_L), however it is unclear if the model generated by Thorsen et al [52] is based on lipid normalised concentration data. Thus *Table 4.19* compares the Log BCF_L model from Geyer et al [17] (*Eqn. 1.4*) and the Log BCF model from Thorsen et al [52] (*Eqn. 4.1*) with the Log BAF_L models generated during this study (*Fig. 4.23a* (n=6 PCBs), *Fig. 4.23b* (n=22 PCBs) and *Fig. 4.24* (n=16 PAH)). The values in parenthesis are the PAH model intercepts when the

models were generated on a wet weight basis, as opposed to lipid weight. The slope remains the same regardless of whether lipid normalisation was completed or not.

Table 4.19: Comparison of Literature Log BCF models with those determined during the course of this study. The PCB slope and intercept values of the present study are presented as values from *Fig 4.23a*. (n=6 PCBs) and (in parenthisis) from *Fig. 4.23b* (n=22 PCBs). PAH values in parenthesis are intercept values from when PAH models are determined on a wet weight basis, as opposed to a lipid basis (*Fig. 4.24*).

Study	Model	PAH/PCB	Location	Slope	Intercept
Present Study				n=6 PCBs (n=22 PCBs)	n=6 PCBs (n=22 PCBs)
	BAF	PCB	Galway	0.83 (1.09)	1.16 (-0.69)
			Dublin	0.73 (1.02)	1.56 (-0.47)
			Native NBL	0.68 (0.93)	1.99 (0.26)
				n=22 PAH lipid/wet wgt	n=22 PAH lipid wgt (wet wgt)
	BAF	PAH	Galway	0.59	1.84 (-0.012)
			Dublin	0.61	1.90 (-0.014)
			Native NBL	0.52	2.33 (0.63)
Geyer et al [17]	BCF	PAH/PCB		0.96	0.22
Thorsen et al [52]	BCF	PAH		0.75	-1.06

Overall the slopes for the lipid normalised equations derived by Geyer et al [17] are similar to those of this study for PCBs, but not for PAHs. Lower PAH slopes were generated from this study as compared to the PAH model from Thorsen et al [52]. However, as Thorsen's study was completed in a flow through system, the potential influence of factors such as particulate organic matter (POM) on contaminant availability would not have influenced their study. It can be concluded that the use of mussel tissue concentrations in combination with PS derived water concentration data can be a powerful tool in the prediction of water concentrations.

4.7.2 Generation of Equilibration Models

In order to investigate if the mussels transplanted from Galway Bay into Dublin Bay reached equilibration during the period of this study, the bioaccumulation factor (BAF) (combination of the accumulation of contaminants from all available compartments), as opposed to the bioconcentration factor (BCF) (dissolved contaminants only) is investigated herein.

Fig. 4.25a (n=6 PCBs), *Fig. 4.25b* (n=20 PCBs) and *Fig. 4.26* (n=15 PAHs) below documents mussel equilibration from initial transplantation from Galway into Dublin Bay. Measurement of the Log BAF_L value of the test mussels over the study period allows for the estimation of the extent of equilibrium reached over the test period. As with the previous generation of models (Section 4.7.1), only compounds for which BAF_L values were available for all samples of interest were included (i.e. n=6 for the Marker PCBs in *Fig. 4.25a* as no BAF_L was available for PCB 28 in the Galway T(start), Dublin T(start) or Dublin T(end) samples). BAF_L values for 15 PAH compounds were available, as are presented in *Fig. 4.26*.

The T = 0 sample refers to the Galway T(start) mussels, collected from the Rinville shoreline (Galway). The Log BAF_L value was determined using PS derived C_w as determined from the Galway PS membrane. The remaining Log BAF_L values were determined using PS derived C_w as determined from the Dublin PS membrane. The T = 26 days sample refers to the Dublin T(start) mussels, which originated in Galway but were equilibrated at the Dublin site for 26 days prior to deployment with the PS device. The T = 70 days sample refers to the Dublin T(end) mussels and the T = unknown (wild) are the Native NBL mussels.

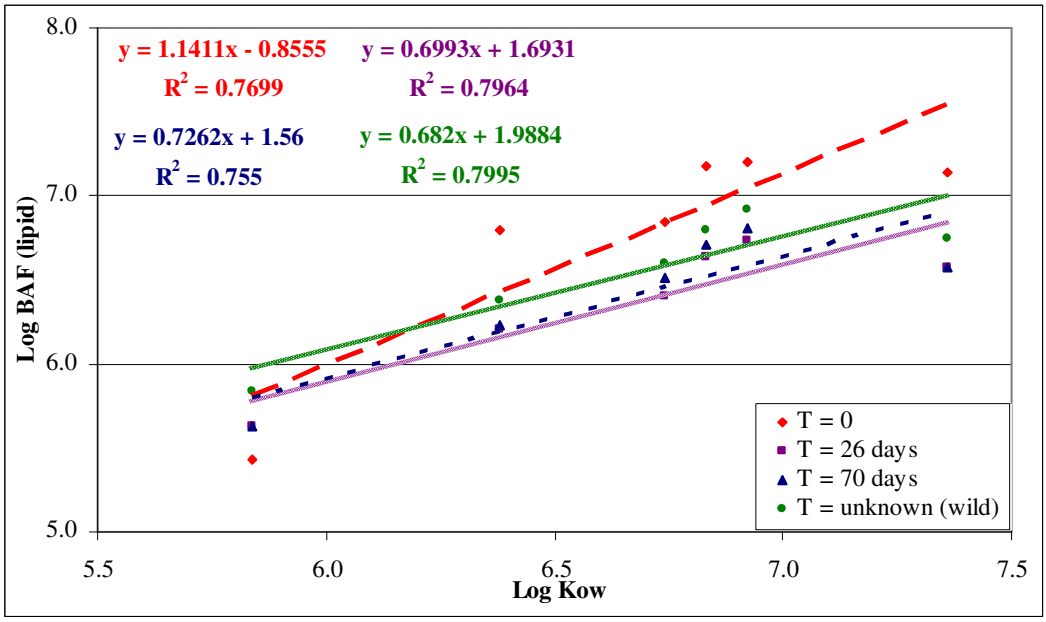

Figure 4.25a: Marker PCB (n=6) Log BAF_L plotted against the Log K_{ow} for Galway T(start): T = 0; Dublin T(start): T = 26 days; Dublin T(end): T = 70 days and Native NBL mussels: T = unknown (wild). These values were determined using PS derived C_w (combined Log $K_{sr,w}$ values)).

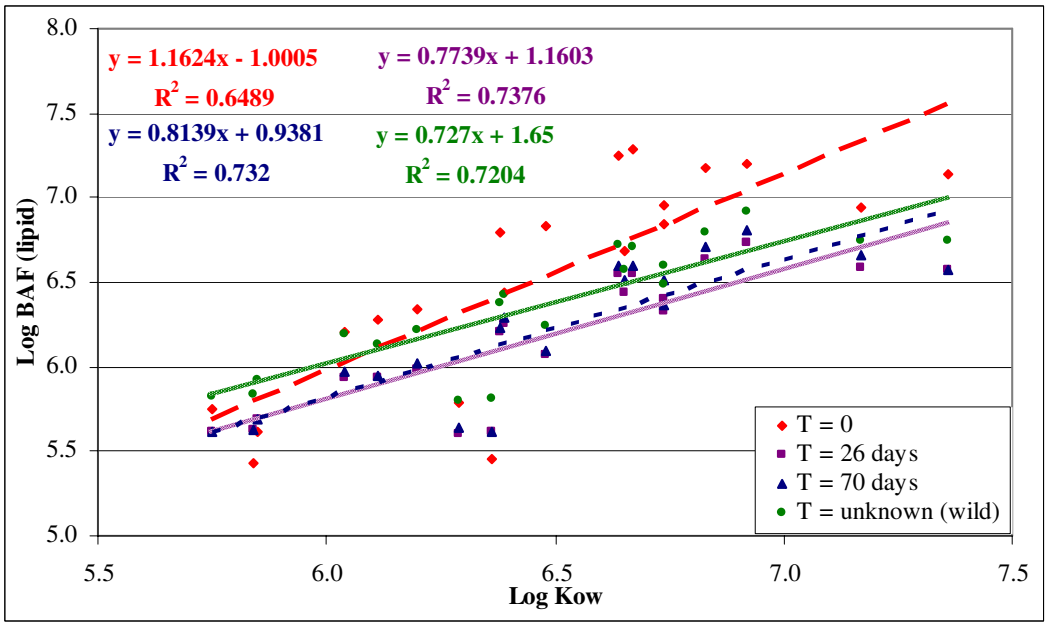

Figure 4.25b: PCB (n=20) Log BAF_L plotted against the Log K_{ow} for Galway T(start): T = 0; Dublin T(start): T = 26 days; Dublin T(end): T = 70 days and Native NBL mussels: T = unknown (wild). These values were determined using PS derived C_w (combined Log $K_{sr,w}$ values)).

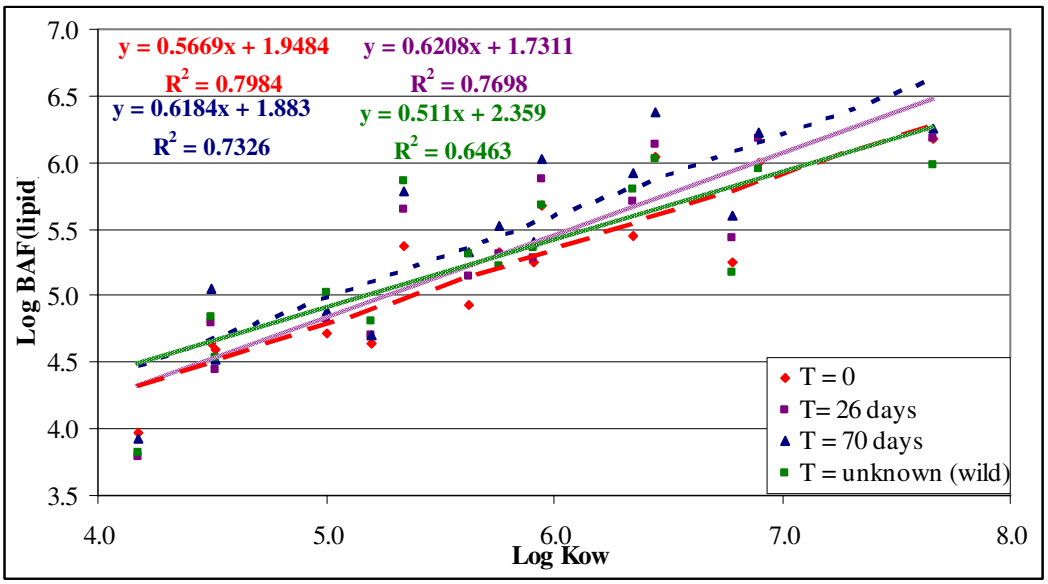

Figure 4.26: PAH (n=15) Log BAF_L plotted against the Log K_{ow} for Galway T(start): T = 0; Dublin T(start): T = 26 days; Dublin T(end): T = 70 days and Native NBL mussels: T = unknown (wild). These values were determined using PS derived C_w (combined Log $K_{sr,w}$ values)).

The mussels originally collected from the Rinville shoreline (T=0 in the above Figures) are considered to be in equilibrium with their local Galway Bay waters, as are the Dublin Native NBL mussels (T = unknown in the above Figures). This Section attempts to determine whether the transplanted Galway mussels completed the equilibrium process to a similar stage as that observed for the Native NBL mussels. This is examined through the comparison of the BAF (lipid weight) Vs Log K_{ow} regression slopes, whereby the T = 70 days slope is compared to the T = unknown (wild) slope, similar slopes being indicative that equilibrium was reached.

In the case of the PCBs (*Fig. 4.25a* and *Fig. 4.25b*), the Galway mussels appear to have reached equilibration after 26 days of the transplantation (*Fig. 4.25a*: T = 26 days slope: 0.6993; T = unknown (wild) slope: 0.682, *Fig. 4.25b*: T = 26 days slope: 0.7739; T = unknown (wild) slope: 0.727), with the slope continuing to rise slightly over the following 44 days (*Fig. 4.25a*: T = 70 days slope: 0.7262, *Fig. 4.25a*: T = 70 days slope: 0.8139).

In the case of the PAHs (*Fig. 4.26*), the original slope of the Galway mussels (0.5669) increased to 0.6208 after 26 days of the transplantation, and decreased to 0.6184 after a further 44 days (T = 70 days slope). The slope decreased with time, however the mussels did not reach the Native NBL level of equilibration during the study period (T = unknown (wild) slope: 0.511).

In short, the data from both *Fig. 4.25a* (n=6 PCBs), *Fig. 4.25b* (n=20 PCBs) and *Fig. 4.26* (PAHs) suggest that after 70 days, the transplanted mussels have reached a similar level of equilibrium to Native NBL mussels (T = unknown).

4.8 References

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CHAPTER 5: CONCLUSIONS OF THE PASSIVE SAMPLING PROJECT AND FUTURE PERSPECTIVES IN PASSIVE SAMPLING

5.0 Introduction

This thesis documents Ireland's participation in the international ICES Passive Sampling Trial Survey (PSTS). As part of this survey, passive sampling of marine waters was completed by thirteen laboratories at up to 31 locations between October and December 2006. European locations covered estuarine and coastal environments from Norway in the north to Portugal in the south, and west to Ireland and the Faroe islands. Two locations in Brisbane, Australia were also sampled.

Primary objectives of this study were to assess the reliability of silicone rubber (PDMS) passive samplers for the measurement of dissolved water concentrations of PCBs and PAHs in the marine water column and to compare resulting data to that obtained from a co-deployed indicator species (*Mytilus edulis*). This thesis reports on the development of the methodologies at two Irish locations and assesses the potential for the future successful applications of passive sampling technologies for the monitoring of hydrophobic pollutants in Irish coastal waters.

This current Chapter condenses the main findings of this thesis into a number of categories by;

5.1 summarising the main analytical and technical deliverables of the project,

5.2 investigating the success of the trial by comparing Irish data to that obtained by other PSTS participants,

5.3 exploring the relevance of such data in light of legislative applications,

5.4 indicating where the data may lead to new perspectives and further research opportunities.

5.1 Technical and Analytical Deliverables

This thesis describes the successful deployment, retrieval and analysis of silicone rubber passive sampling membranes at two test locations in Irish coastal waters, namely, at the North Bank lighthouse in Dublin Bay and at Rinville in Galway Bay. PS devices in combination with transplanted mussels were co-deployed between the $6^{th}/7^{th}$ of November and the $19^{th}/20^{th}$ December 2006.

This Section is thus divided into the following:

5.1.1 Deployment and retrieval.

5.1.2 Biological aspects.

5.1.3 Chemical aspects.

5.1.4 Modelling and contaminant profiling techniques.

5.1.1 Deployment and Retrieval

The PSTS trial protocol essentially amounted to the development of methodologies that would allow mussels (*Mytilus edulis*) to be placed in a basket at the base of the PS frame and to be co-deployed with the actual silicone rubber passive sampling membranes. In order to minimize the potential for size related differences in contaminant uptake/metabolism within the mussels (and between locations), a standardized approach was developed for the collection and selection of mussels used for this study, whereby only size classed (40-60mm) mussels collected from a designated "reference" site (Rinville Co. Galway) were used for the transplantation study. Appropriate mussels were then transported to the two Irish test sites, where deployment of the PS devices was successfully completed.

Deployment for the 6 week test period involved securing the sampling frames (with the silicone rubber membranes and basket of mussels attached) to permanent moorings at the two test sites; the Dublin frame being secured (via teflon ropes and cable ties) to one of the fixed supports of the Northbank Lighthouse (NBL) while the Galway frame was attached to a permanent navigation buoy located at Rinville point.

After the deployment period the devices were returned to the laboratory where they were disassembled, membranes removed and prepared for analysis. Viable mussels were selected and whole soft body tissues of 50/60 individuals was pooled, homogenized and stored at -30 ^{o}C prior to analysis.

Successful analysis under subcontract was completed on a range of analytical matrices (spot water samples, passive sampling devices and transplanted and native mussels) for both PCBs and PAHs, while supporting biological parameters and normalisation co-factor (lipid, moisture and condition index) analysis was completed on all mussel samples. Results of biological and chemical deliverables are further summarised below.

5.1.2. Biological Aspects

The lipid content of the Native NBL mussel sample is almost twice that of the Dublin T(end) sample, which may help to explain why the majority of the PCBs measured in NBL mussels are in excess of twice the levels detected in the Dublin T(end) sample. Lipid (and dry weight) normalisation procedures were developed and incorporated into data assessment as appropriate in order to minimise the effects such natural/biological variation may have on comparison of test results between locations.

Experimental and field studies have demonstrated that it may take 40-90 days to reach equilibrium between PAH concentrations in mussels and the environment [1, 2]. This time period is concurrent with the exposure period of test mussels transplanted from the Galway to Dublin site (i.e. 26 day equilibration and 44 day deployment = 70 days). Such "equilibration" observations are further discussed below.

The condition of the Dublin transplanted mussels at the end of the exposure study [C.I.=10] was found to be slightly lower than their Galway counterparts [C.I.=13], possibly indicating that the mussels found it difficult to adjust to conditions in Dublin Bay compared to their original site. Native Dublin Bay mussels exhibited a greater overall condition index [C.I.=16] compared to all other mussels tested. Overall it was determined that while the condition index of mussels transplanted to Dublin was found to be lower than those at the Galway location, they were still biologically viable at the end of the study and thus were suitable for use for analytical analysis.

This study has additionally concluded that the derivation of such proxy condition indices is a valuable indicator of the relative success of transplantation experiments and that where possible the organisms selected for transplantation purposes may potentially be best sourced at locations with similar salinity ranges and particulate matter types and loadings, thus reducing the potential for stress on transplanted animals.

5.1.3 Chemical Aspects

Passive sampling has been defined as a chain of actions and calculations using various constants (each with their uncertainty) that yields an estimate of the freely dissolved aqueous-phase concentration [3]. Throughout this thesis the concepts and successful application of the use of performance reference compounds (PRCs) has been

documented, this having proved to be a valuable concept to allow for the derivation of membrane sampling rates and consequently dissolved contaminant levels as further discussed below.

While this thesis reports a mechanism to select appropriate PRCs that ultimately provided dissolved water contaminant levels within similar ranges to those of the central reference laboratory, it must be noted that the PRC concept is in its relative infancy and selection of appropriate PRC compounds continues to be a work in progress.

While individual participants conducted their own fieldwork and laboratory analysis, duplicate samples were analysed by a single coordinating, reference laboratory. Papers presented at the 2007 ICES Annual Science Conference showed that the repeatability of sampling results and agreement between laboratories were good [(4)].

Overall it was concluded from this present study and the overall PSTS exercise that silicone rubber passive sampling enables the dissolved water concentrations of contaminants to be measured down to the level of picograms per litre, an impractical task by standard/classical sampling [(5)].

Further chemical aspects and summary conclusions from the analysis of each of the individual matrices (spot water samples, mussels and passive sampling devices) are further described below.

5.1.3.1 Analysis of Spot Water Samples

An assessment of PCB levels was only possible in the Galway sample as PCBs were not detected in the Dublin spot water sample i.e. all concentrations fell below the LoQ values. Overall PCB concentrations in the Galway Spot water sample were low, (21 compounds were not detected below their LoQ) with the majority of those determined having concentrations <100 pg/l.

As analysis was completed on unfiltered spot water samples, the analytical results obtained via the spot water and the passive samplers are not fully comparable. Results do suggest however that the LoQs of the PS derived water concentrations may potentially be an order of magnitude lower than those of the spot water samples e.g. LoQ for PCB 157: 62 pg/l (Spot) Vs 0.25 pg/l (PS) and PCB 189: 3.00 pg/l (Spot) Vs 0.11 pg/l (PS). Thus this technique may be viable for use in marine waters where pollutants are only present at ultra trace levels.

As regards PAHs, in general, the concentrations of individual PAHs measured in the spot samples are greater in Dublin than those in Galway. All 16 US EPA PAHs are present in the Dublin spot water sample at concentrations of >1 ng/l, with the exception of dibenzo[a,h]anthracene (0.35 ng/l). The increased level of suspended particulate matter in the Dublin water sample may partially account for the greater representation of the heavier molecular weight compounds.

5.1.3.2 Analysis of Test Mussel Samples

Dry weight concentrations of a number of lower chlorinated marker PCBs (PCB 28 and 52) plus some lower "other" PCBs (PCB 33, 41, 44, 47, 49, 51, 61, 66) were greater in Galway mussels analysed at the end of the exposure study than those in the Galway

T(start) sample, while the reverse was true for the remaining five marker PCBs and the majority of the remaining "other " PCBs. In contrast, the concentration of all marker PCBs and the vast majority of the "other" PCBs were greater in the Dublin T(end) mussels than the T(start) mussels.

Although the majority of the higher chlorinated "other" PCB compounds (with 5 or more chlorine atoms), were found to be comparable between the start and end of the exposure study at both sites, the concentration patterns differ as follows: the concentrations in the mussels at the Galway site decrease with time, while those at the Dublin site increase.

The reduction in levels observed at the Galway site may be as a result of lower bioavailability of these compounds to the mussels, lower contaminant levels, seasonal variations *etc* or (as is less likely) may potentially indicate an ability for the mussels to metabolise/deplete/excrete these PCBs from their mussel tissues during the deployment period, however this would require further investigation.

PCB levels generally increased in mussels transplanted to Dublin Bay indicating either greater bioavailability and/or contaminant levels at the NBL site. PCB concentrations were found to be greatest in the Native NBL mussels compared to those transplanted to the Dublin test site. It should also be noted that the Native NBL mussels display both the highest lipid content and C.I. compared to other mussels tested and that further normalisation or profiling techniques may need to be considered in future PS trials to account for such biological variation. Whether the Native NBL mussels contain the highest level of contaminants as a result of their high lipid content, or have the highest lipid content as a result of the continuous exposure to contaminants remains unclear.

Overall, the most abundant PAHs in the mussel samples were found to be pyrene, fluoranthene, phenanthrene, chrysene-triphenylene, benzo[b+j+k]fluoranthene and benzo[e]pyrene. In general, PAH concentrations in the T(end) mussel samples were greater than those in the T(start) mussel samples at both the Galway and Dublin sites, indicating that bioaccumulation occurred during the deployment period.

Mussels transferred to the Northbank lighthouse rapidly accumulated PAH during the initial 26 day equilibration period, demonstrating that a number of PAH compounds were bioavailable at the Dublin test site. The accumulation of the tetra aromatics (from petroleum) was additionally evident (See Section 5.1.4).

5.1.3.3 PS derived Water Concentrations

The PSTS study required the use of a number of standardised formulae for the derivation of dissolved water concentrations of contaminants. A number of factors (variation of Log $K_{sr,w}$ values, R_S values and membrane contaminant concentrations) potentially influencing passive sampling derived dissolved water concentrations of PAHs and PCBs were investigated in order to evaluate the potential effects these had on derived concentrations.

Sampling rate (R_S) determined by the MI for both Galway and Dublin were lower than those determined by the Reference Laboratory. While the Galway R_S values determined by both laboratories were found to be relatively similar (8.48 l/d (MI); 10.2 l/d (Ref)), the Dublin R_S determined by the MI (2.38 l/d) is almost half that determined by the Reference laboratory (4.93 l/d). Such differences may ultimately contribute to the fact that PAH concentrations as reported by the MI for both sites were consistently higher than those reported by the central reference laboratory, (exception acenaphthene).

Overall dissolved water concentrations as derived by both the MI and the reference laboratory were found to be relatively comparable and given that response factors, recovery rates, selection of reference compounds and analytical techniques (amongst other variables) will differ between laboratories that the technique can be considered to be relatively robust for the purposes of water monitoring.

Dissolved PCB water concentrations as determined from the Dublin PS were found to be consistently higher than those reported for the Galway PS. In general, the dissolved water concentration of PCB congeners decreased with increasing degree of chlorination, with the overall congener profile being similar at both sites.

With the exception of naphthalene, PS derived PAH C_w were found to be consistently higher at the Dublin site than at Galway, with the PAH profile in the Dublin sample exhibiting greater relative concentrations of higher condensed PAHs compared to Galway.

5.1.3.4 Concentration Patterns

While up to this point the contaminant concentrations as determined from the mussel tissues (µg/kg dry weight) and the PS (pg/l PCBs; ng/l PAHs) have been discussed independently of each other, this current section outlines the similarities and differences in the patterns observed between the mussel concentrations and the PS derived C_w as determined from each site. As the mussel concentrations and the PS derived C_w are not expressed in the same unit, they therefore cannot be expressed on a single plot or directly compared. For this reason, the PCB data (WHO and Marker) are presented on two separate plots (*Fig. 5.1* and *Fig. 5.2*), as are the PAH data (US EPA PAHs) (*Fig. 5.3* and *Fig. 5.4*). The concentrations of all PCB and PAH data depicted in the figures

below are given on a Log(x+1) basis, thus enabling the graphical presentation of both high and low concentrations on the individual graphs.

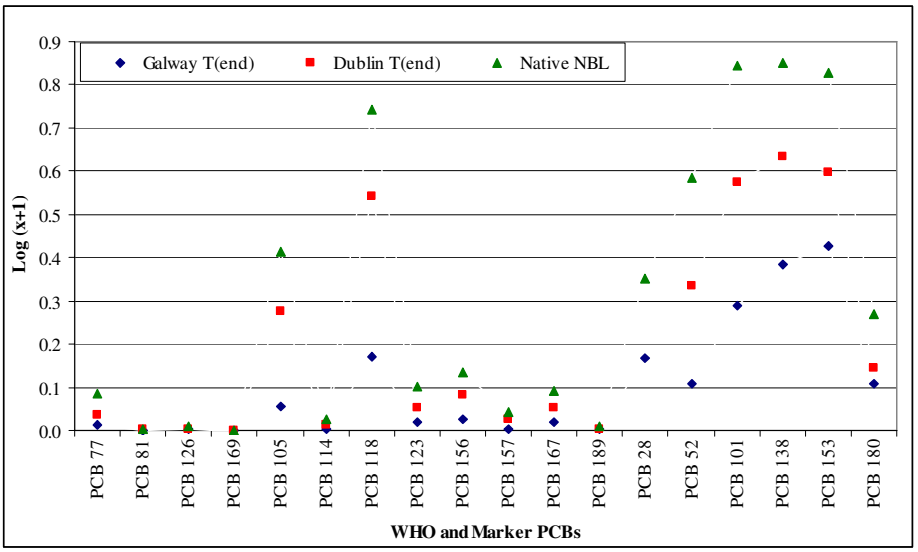

Figure 5.1: WHO and Marker PCB concentrations (µg/kg dry weight) (Log(x+1)) in T(end) mussel samples taken from both the Galway and Dublin sites and the Native NBL mussel concentrations.

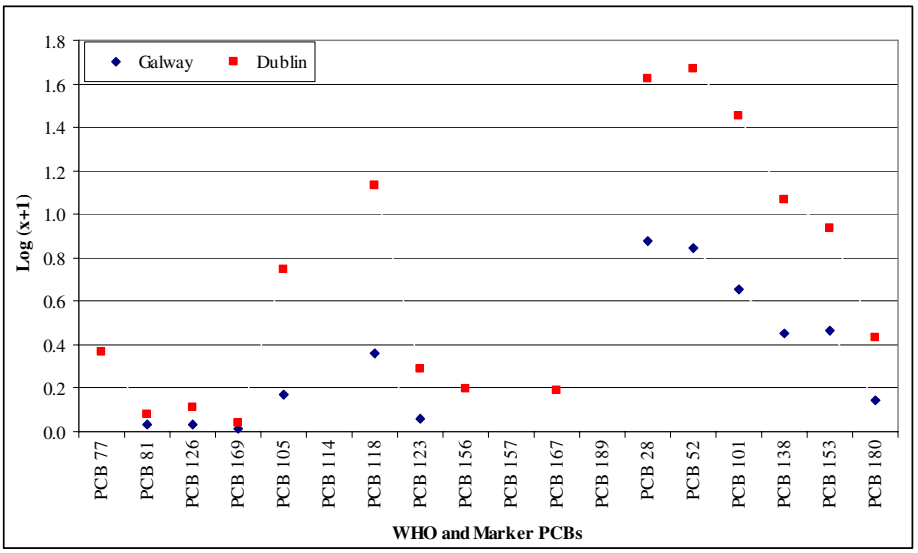

Figure 5.2: PS derived WHO and Marker PCB concentrations (pg/l) (Log(x+1)) in Galway and Dublin as determined using a combination of literature (where available) and estimated Log $K_{sr,w}$ values.

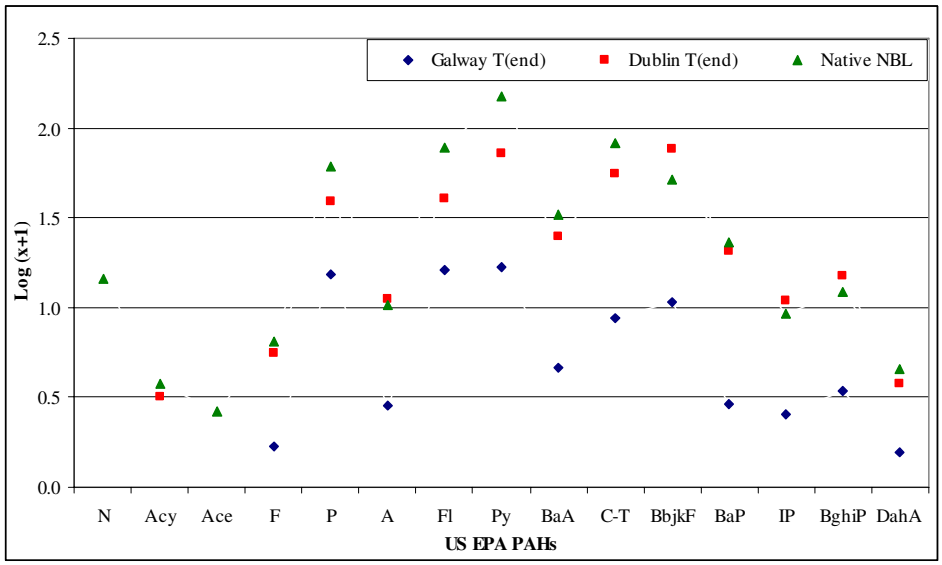

Figure 5.3: US EPA PAH concentrations (µg/kg dry weight) (Log(x+1)) in T(end) mussel samples taken from both the Galway and Dublin sites and the Native NBL mussel concentrations.

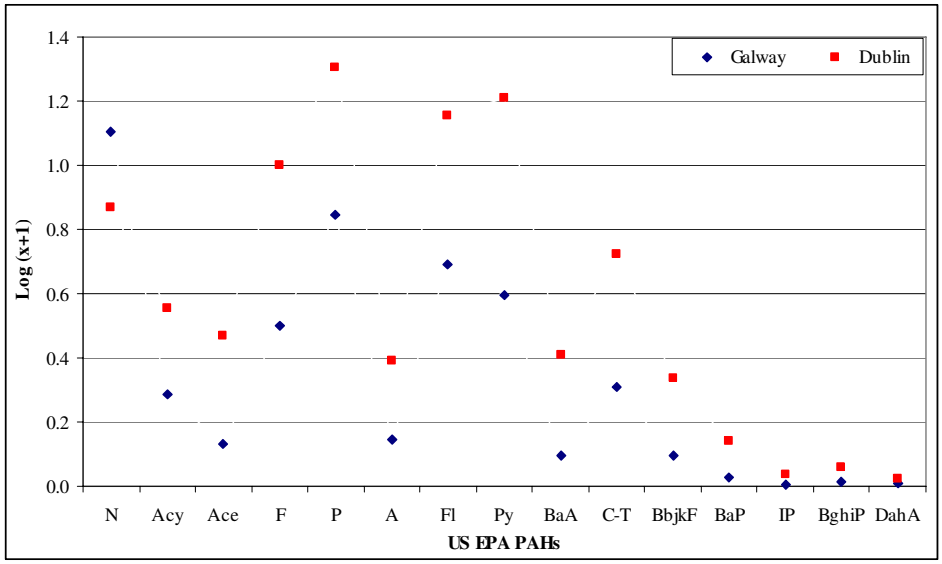

Figure 5.4: PS derived US EPA PAH concentrations (ng/l) (Log(x+1)) in Galway and Dublin as determined using a combination of literature (where available) and estimated Log $K_{sr,w}$ values.

The PCB concentrations as determined from both media (mussels and PS) are higher in the Dublin samples than those from Galway. The WHO PCB concentrations in *Fig. 5.1* and *Fig. 5.2* follow a general pattern whereby compounds which have high PS derived C_w have correspondingly high mussel concentrations e.g. WHO PCB 105 and PCB 118. This is not surprising, given that mussels accumulate most of their contaminant loading from the dissolved phase in low turbidity waters (Galway: 5 mg/l; Dublin: 20.6 mg/l).

In general, the Marker PCBs are found in higher concentrations than the WHO PCBs in both media (PCB 118 falls into both categories). However although the Marker PCB concentrations in both media are high, the concentrations increase with increasing molecular weight in the mussels, with the reverse occurring in the PS derived C_w. This may indicate the ability of mussels to accumulate higher molecular weight (lower water solubility) compounds from sources other than the dissolved phase i.e. food and sediment.

Similar to the PCB concentration pattern, the PAH concentrations as determined from both media are higher in the Dublin samples than those from Galway (*Fig 5.3* and *Fig. 5.4*). The lower range PAH compounds (high water solubility) are well represented in the water samples (PS), but many are absent in the Galway and Dublin T(end) mussels. This may potentially indicate an ability for mussels to metabolise/deplete/excrete these PAHs. The mid range molecular weight PAHs are well represented in both the mussel tissues and the PS, reinforcing the importance of dissolved phase contaminants in the contaminant loadings of marine biota.

PAH water solubility decreases with increasing molecular weight, thus accounting for the low levels of high molecular weight compounds as determined by the PS (*Fig 5.4*). However, the presence of such high molecular weight compounds in the mussel tissues suggest that, like the higher chlorinated PCBs, the mussels are obtaining such contaminants (low water solubility) from sources other than the dissolved phase i.e. particulate or colloidal phases.

5.1.4. Modeling and Profiling Techniques

This study was designed in a way that further modelling and profiling techniques could be incorporated into result assessment, these were categorised as follows;

5.1.4.1 Estimation of Log $K_{sr,w}$ values for use in the absence of literature values.

5.1.4.2 Bioaccumulation factor modelling, using mussel tissue concentrations and PS derived water concentration information.

5.1.4.3 Transplantation equilibration models.

5.1.4.4 PAH ratio profiling of data from individual matrices.

5.1.4.1 Estimation of Log $K_{sr,w}$ Values for use in the Absence of Literature Values

While a number of Log $K_{sr,w}$ values are currently available in the literature for use in the determination of dissolved water concentrations, a great number have yet to be analytically determined. In the course of this work literature Log $K_{sr,w}$ values were regressed against literature Log K_{ow} values in order to derive a model suitable for the estimation of Log $K_{sr,w}$ where only Log K_{ow} information were available. The majority of differences between the PCB water concentrations derived using estimated Log $K_{sr,w}$ and those derived using literature values were found to be in the order of <1 % (pg/l).

The use of estimated Log $K_{sr,w}$ values was found to result in a lower C_w for approximately half the PCBs and in higher water concentration for the remaining PCBs. The maximum differences in water concentrations determined using estimated Log $K_{sr,w}$ values were found to range from 8.00 % less than (PCB 31) to 3.18 % greater than (PCB 44) those determined using literature Log $K_{sr,w}$ value. The use of estimated $K_{sr,w}$ values was found to be prone to greatest error for lower Log K_{ow} ($K_{sr,w}$) PAHs. Overall the use of either literature or estimated $K_{sr,w}$ values was found to be suitable for the derivation of PS C_w for the majority of PCBs and higher condensed PAHs.

It was additionally concluded that when using literature Log $K_{sr,w}$ values [6, 7] , the percentage difference in dissolved water concentrations increases with decreasing molecular weight. Since a decrease in molecular weight relates directly to a decrease in Log $K_{sr,w}$ value, the impact of varying the Log $K_{sr,w}$ value on the determination of the C_w therefore becomes more evident at higher molecular weights.

5.1.4.2 Bioaccumulation Factors (BAF)

Side-by-side deployment of PS devices and mussels allow for comparison of contaminant uptake by the PS (truly dissolved contaminants) with the concentrations found in the organisms (contaminants in dissolved, particulate and colloidal forms) from the same site. The data obtained from the analyses of contaminant concentrations in the mussel tissues and the freely dissolved water concentrations derived from the PS membranes from each location were then used to calculate the bioaccumulation factors (BAF) for each compound (See Section 4.7.1).

As regards the Irish data, a selection of the PCB and PAH Log BAF models generated during the course of this study were compared with existing BCF models from Geyer et al [8] (PCB) and Thorsen et al [9] (PAH). While similar PCB slopes (n=6: 0.83 (n=22: 1.09) for Galway, n=6: 0.73 (n=22: 1.02) for Dublin and n=6: 0.68 (n=22: 0.93) for the Native NBL mussels) were generated from this study as compared to Geyer et al [8] (0.96), lower PAH slopes (0.59 for Galway, 0.61 for Dublin and 0.52 for the Native NBL mussels) as compared to Thorsen et al [9] (0.75) were experienced. This discrepancy may relate to the means in which the BAF was calculated i.e. mussels were exposed solely to dissolved PAH in a controlled flow through system by Thorsen et al [9], whereas the mussels in this present study were exposed to a real life environment where PAH bioavailability was affected by factors such as particulate organic matter.

The BAF model derived in this present study (using PAH and PCB data, *Fig. 5.5*) additionally appears to be consistent with that within the greater scope of the PSTS study (See *Fig 5.6*).

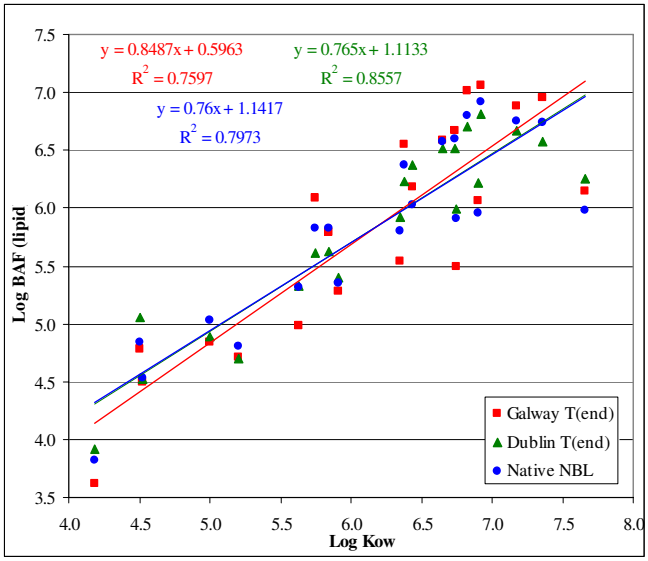

Figure 5.5: Relationship between Bioaccumulation Factors calculated by the present study from freely dissolved concentrations of PAHs and PCBs in water (PS derived) and concentrations in Galway T(end), Dublin T(end) and Native NBL mussel tissues and Log K_{ow} values.

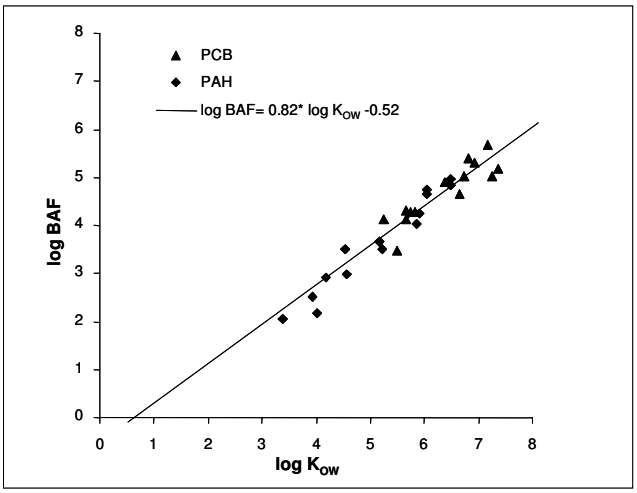

Figure 5.6: Relationship between Bioaccumulation Factors calculated by the PSTS from freely dissolved concentrations of PAHs and PCBs in water (PS derived), concentrations in mussel tissues and Log K_{ow} values. (Graphic reproduced from Smedes et al [(4)].)

The 75% trimmed mean of the calculated BAFs for the PAH, HCB (Hexachlorobenzene) and PCB compounds for mussels from the PSTS survey were plotted against the Log K_{ow} for these compounds (*Fig 5.6*). Although the actual data is not available, according to Smedes et al [(4)], the linear relationship obtained appeared to

be consistent with the model developed by Bergen et al [10] (i.e. Log BCF = 0.82 Log K_{ow} - 0.52). The Irish data (*Fig. 5.5*) is also in agreement, with slopes of 0.85 for Galway, 0.77 for Dublin and 0.76 for the Native NBL mussels.

The PSTS data indicate that silicone rubber passive sampling of water can be used to predict the concentrations of PCBs and PAHs in mussels over a range of Log K_{ow} from about 3.2 to 7.8.

Overall, in line with the other PSTS participants, it can be concluded that the use of mussel tissue concentrations in combination with PS derived water concentration data can be a powerful tool in the prediction of water concentrations.

5.1.4.3 Equilibration Models

Mussels can bioconcentrate/bioaccumulate contaminants from the water column. However, if exposure to aqueous (dissolved and particulate) concentrations of PAHs decreases, mussels may depurate the absorbed PAHs back to the water phase [11]. Thus at any given time, the steady-state concentration of PAHs in mussels at a given location reflects the inputs of bioavailable PAH sources. An investigation was completed into developing a methodology capable of determining whether the transplanted mussels completed the equilibrium process at the Dublin bay site.

At three stages throughout the deployment, mussels transplanted to Dublin bay were sub-sampled and used for model generation. The slopes of the derived models were then directly compared to native mussels which were collected from the NBL support legs. These similar sized Native NBL mussels were assumed to have reached equilibrium with their environment. The equilibration model was generated through the comparison

of the BAF (lipid weight) Vs Log K_{ow} regression slopes, whereby the Dublin T(end) mussel slope was compared to the Native NBL mussel slope. The data obtained from this investigation suggest that after 70 days, the transplanted Galway mussels reached a similar level of equilibrium to Native NBL mussels for both PCBs and PAHs.

While the use of such approaches would require further validation, to the best of the author's knowledge, no similar approaches to monitor transplantation success and the stage of equilibrium are available in the literature.

5.1.4.4 PAH Ratio Profiling of Data from Individual Matrices

PAH profiling can provide a powerful mechanism to further describe the potential sources of PAHs in the environment. Deriving information from suitable ratios can assist in deciding whether the likelihood of PAHs in a matrix originated from petrogenic, pyrogenic and/or biogenic sources. It should be noted that definitive source identification is not possible from PAH ratios alone (especially close to "cut-off" values) and the potential for metabolic/excretion capabilities in addition to mixed source influences must additionally be addressed when completing such assessments.

The PAH ratios (P/A and Fl/Py) determined from the Galway passive sampling membranes and both Galway (Tstart and Tend) mussel samples indicate a mixed sources of PAH at the Galway site. No comparable ratios were available for the Galway spot water sample, as 3 of the 4 isomers required to generate an index were not detected in the water sample. The IP/(IP + BghiP) ratio from the passive sampling membrane and both mussel samples are in agreement, primarily indicating the influence of petroleum combustion sources. However, while the PS and the T(start) Fl/(Fl + Py) ratio indicate biomass and coal combustion and both A/178 ratios indicate unburned petroleum, the

T(end) ratios indicates petroleum combustion and combustion sources respectively. As regards the BaA/228 ratio, both Galway mussel sample indicates a mixed PAH source from both petroleum and combustion while the passive sampling membrane BaA/228 ratio indicated unburned petroleum.

The PAH ratios (P/A and Fl/Py) as determined from all three Dublin mussel samples indicate a mixed source of PAH, with the passive sampling membrane indicating the influence of petrogenic sources while the spot water sample additionally indicates the influence of pyrolytic sources. The BaA/228 and IP/(IP + BghiP) ratios determined in all three Dublin mussel samples and the passive sampling membrane are in general agreement, indicating mixed sources of PAH from petroleum and combustion and petroleum combustion respectively. The A/178 ratios from all three mussel sample indicate combustion sources while that from the PS indicates unburned petroleum. The Fl/(Fl + Py) ratios were found to differ slightly between the mussel samples, with the Dublin T(start) mussels indicating a petroleum combustion source while the Dublin T(end) and Native NBL samples indicate the influence of unburned petroleum. The passive sampler ratios indicate biomass and coal combustion, which would be consistent with the presence of the adjacent power generation facility.

Although the three matrices analysed (i.e. spot water, PS and mussels) were not always in agreement on the sources identified by individual ratios, it can be concluded overall that the PAH from both sites are the result of a mixture of petrogenic and pyrogenic sources.

5.2 Investigation into the success of the passive sampling trial by comparing Irish data to that obtained by other PSTS participants

To date, only summary details documenting the overall success of the PSTS exercise are currently available [4].

In the case of PAHs it can be concluded that,

- PS derived water concentrations for individual PAHs ranged over 3 orders of magnitude, with highest PS derived PAH C_w determined from the Karmoy site in southwest Norway where aluminium smelters in the area are known sources of aqueous discharges containing PAHs (particularly the heavier compounds).
- The PS derived C_w of the lighter PAHs (e.g. phenanthrene (*Fig. 5.7*)) in far west stations (Ireland, Scotland and the Faroe islands) appear to be as high as those in areas of the SE North Sea, where concentrations might be expected to be higher. This may reflect high concentrations of suspended particulate matter (SPM) in the southern North Sea adsorbing PAHs and reducing the dissolved concentrations, whereas atmospheric inputs in the west occur into water with low SPM and thus higher concentrations may remain in solution.
- Concentrations of the heavier PAHs are lower at the western stations (Ireland, Scotland and the Faroe islands) than in the southern North Sea, except in relatively enclosed harbours such as Aberdeen (Scotland) and Dublin (Ireland) where dissolved concentrations are higher and may reflect local inputs.
- In the outer parts of the Scheldt, PS derived water concentrations of lighter PAHs (e.g. phenanthrene (*Fig. 5.7*)) increase seawards, which may reflect the significance of atmospheric inputs of PAHs. In contrast, the heavier PAHs (e.g. benzo[a]pyrene (*Fig. 5.8*)) tend to show progressively decreasing concentrations towards the open sea.

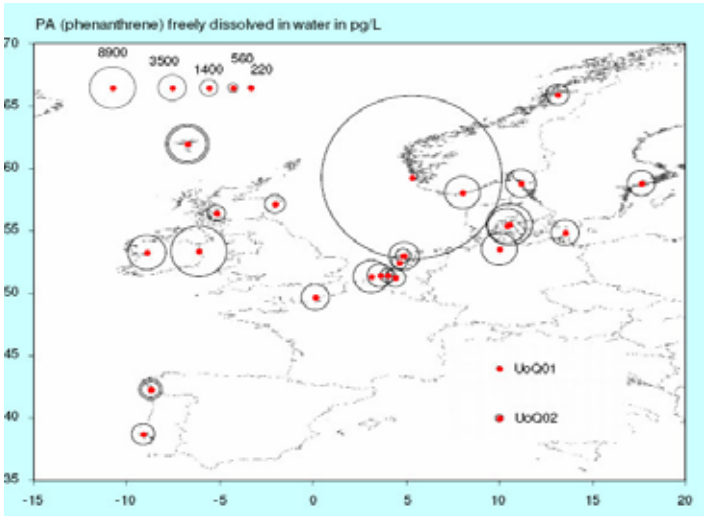

Figure 5.7: PS derived water concentrations of phenanthrene (pg/l), as determined by the Reference Laboratory for each of the PSTS sampling locations. (Graphics from Smedes et al [4])

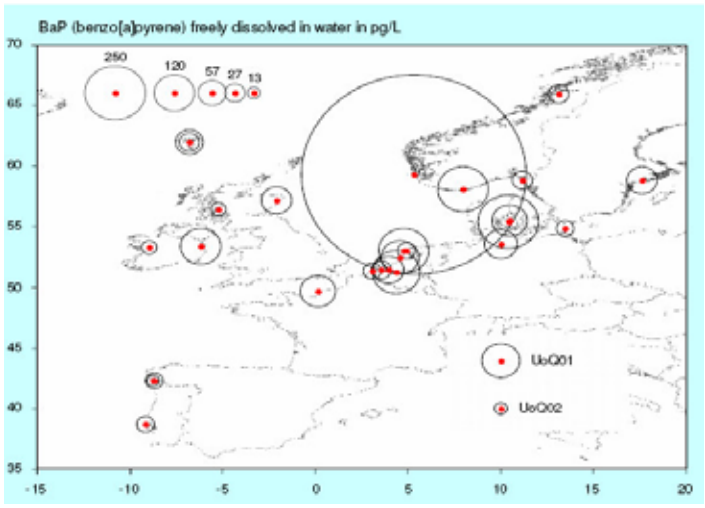

Figure 5.8: PS derived water concentrations of benzo[a]pyrene (pg/l), as determined by the Reference Laboratory for each of the PSTS sampling locations. (Graphics from Smedes et al [4])

With respect to PCBs it can be concluded that;

- PS derived PCB water concentrations at sampling stations in Norway and the western locations (Ireland, Scotland and the Faroe Islands) are low in comparison to those found at sites on the southern coast of the North Sea (*Fig. 5.9* and *Fig. 5.10*), the reason being that there are no large local inputs, and possibly no significant atmospheric inputs, in these areas.
- The high concentrations in the inner Scheldt decrease seawards, possibly reflecting the dilution of river water by open sea water.

- PCB concentrations are also high in the Seine estuary (France).
- While concentrations of light PCBs are low at Vigo (Spain), concentrations of more heavily chlorinated PCBs (e.g. PCB 153 (*Fig. 5.9*) and PCB 187 (*Fig. 5.10*)) are relatively high in comparison to concentrations at other sites.

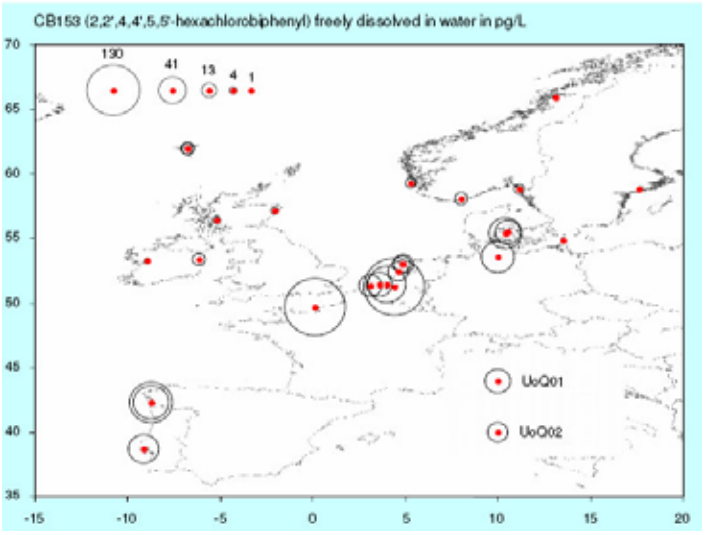

Figure 5.9: PS derived water concentrations of PCB 153 (pg/l), as determined by the Reference Laboratory for each of the PSTS sampling locations. (Graphics from Smedes et al [4])

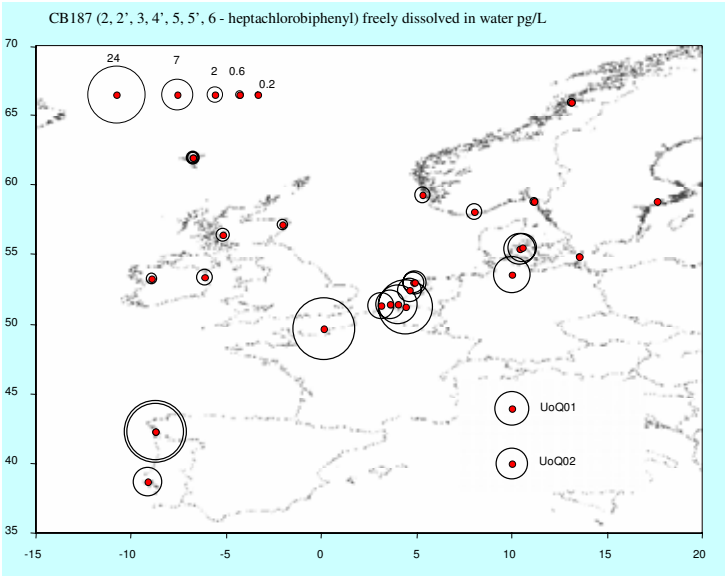

Figure 5.10: PS derived water concentrations of PCB 187 (pg/l), as determined by the Reference Laboratory for each of the PSTS sampling locations. (Graphics from Smedes et al [4])

Overall, it can be concluded that PAH and PCB data generated during this study are in line with those derived by similarly located PS devices and the trial has generally been deemed a successful exercise.

5.3 Legislative Considerations

The European Union's Water Framework Directive (WFD; 2000/60/EC) [12] is one of the most important pieces of environmental legislation of recent years and will potentially transform the general thinking on how water quality monitoring is undertaken in the future. The WFD applies to most types of water body (ground, coastal, transitional and surface waters) and it aims to achieve "good quality" status of all water bodies by 2015. For the successful implementation of the WFD it will require the development and use of alternative 'emerging' and low-cost monitoring methods [13, 14]. These methods may be used to complement monitoring already in place (e.g. spot, grab or bottle sampling followed by analysis in the laboratory using classical methods) by providing additional, more representative, information on the status of a water body. Each type of monitoring (i.e. investigative, operational and surveillance) specified within the WFD will require a set of fit-for-purpose 'tools' that can provide meaningful and reliable data.

The Water Framework Directive (WFD) list of Priority Pollutants includes those that are known to be particularly harmful to the environment and/or to resident organisms [13]. The monitoring of such priority substances in surface and coastal waters, sediment and biota forms an important part of protecting the water environment to ensure that water is managed in a sustainable manner that ensures sufficient water of suitable quality for all users. The low concentrations of some of these priority pollutants, now known to have biological effects, requires the development of suitable analytical methodologies to allow cost-effective and rapid monitoring of the water environment. The legal basis of the overall directive will be primarily linked to reporting of data, which should be of demonstrated and comparable quality throughout the European Union [15]. The WFD does not mandate any particular method of monitoring or chemical

analysis, but requires that comparable methods, both of sampling and analysis, be used with good accuracy and precision so that differences between water bodies and trends can be detected reliably. The monitoring should support the establishment of a coherent and comprehensive overview of water status within each river basin district [13].

Some of the emphasis has been on checking compliance with environmental quality standards (EQSs) in waters by means of spot or grab sampling combined with classical laboratory analysis for which well-established protocols are available. However, monthly (or less frequent) spot samples at a few fixed sampling stations may not provide an adequate picture of water quality where there are marked variations in space (for instance due to pressures such as discharges or run-off), or in time due to, for instance, seasonal agricultural applications of pesticides, or sporadic industrial discharges, or weather dependent run-off from roads or fields. High frequency spot sampling is very costly because of the labour and transport involved, and increasingly alternative methods of monitoring are being considered [13].

Passive sampling technologies were developed to measure Time Weighted Average (TWA) concentrations of pollutants in air, and in water and have the potential to mimic bio-monitoring where uptake by living organisms is measured and provides a good measure of the biologically relevant concentration of pollutants [13]. While biomonitoring has been used in a number of countries (incl. Ireland) as part of routine monitoring programmes in coastal waters, passive sampling has only been utilised to support such programmes in a limited number of countries (e.g. The Netherlands and Belgium) [5].

Passive sampling may prove useful in monitoring programmes in support of the WFD, which will require relevant monitoring data for better risk assessment of pressures, identification and follow-up of the efficiency of programmes of measures, and compliance checking (based on EQS and Groundwater Quality Standards). Currently passive sampling technologies provide an opportunity to obtain representative reliable information that could be used to support robust risk analyses, and may assist in the avoidance of the potential high costs incurred of making inappropriate responses on the basis of spot sample data collection.

While a number of research goals need to be fully addressed with regard to the wider scale application of passive sampling methodologies (e.g. validation of suitable PRCs for a range and spread of water solubilities), passive sampling shows promise as a reliable, robust tool that can provide biologically relevant information on pollutant concentrations in a cost-effective manner in a wide range of aquatic environments

Smedes et al [(4)] report that an accurate and reliable means of measuring concentrations of organic marine contaminants remains a major challenge in controlling pollution in the sea. That challenge is now even more pressing with the EU's agreement on the Marine Strategy Framework Directive [(16)], which aims to ensure healthy European marine waters by 2020, through protection and preservation of the marine environment. Smedes et al [(5)] suggest that passive sampling is currently, the most promising means of monitoring the availability of such persistent organic pollutants, and particularly their potential availability to other organisms in the sea.

The key measure of contaminant availability lies in their "freely dissolved concentration", but, because of the almost complete insolubility in water of such hydrophobic pollutants, the actual dissolved concentrations are generally very low. Thus, the evidence from the ICES PSTS trial suggests that passive sampling does indeed have huge potential in monitoring marine pollution from hydrophobic organic compounds, particularly concerning their availability to organisms.

Because the EU's new Marine Strategy Framework Directive is likely to require contaminant measurements at very low concentrations in open sea areas, passive sampling seems set to become a key tool for marine chemists and toxicologists. As yet, passive sampling (as reported in this thesis) is the only way to assess the low concentration requirements for good environmental status assessment [(5)].

5.4 Future Work/Perspectives

Throughout this thesis the potential for the application of passive sampling methodologies to support environmental monitoring has been established. The technique is in its "relative" infancy compared to "conventional" analysis methodologies; as such scope exists for further research in the area, including;

1. Development of the PRC method as utilised in this study in order to further validate sampling rates.
2. Further develop equilibration modeling to support analysis and assessment.
3. Analysis of filtered spot water samples in order to determine truly dissolved contaminants. This would then allow direct comparison of the bioavailable contaminant levels as determined from (filtered) spot water samples and PS.
4. Future trials encompassing a variety of passive samplers for the detection of a broad range of pollutants.
5. Complete "offshore" passive sampling trials to determine "background" water concentrations in order to further support the development of legislative assessment criteria.
6. Further investigate the use of passive sampling to provide "environmentally derived" pollutant extracts for use in toxicological bioassays.
7. Investigate the potential use of bioindicator derived BAF models in order to predict water concentrations where only tissue contaminant levels and the Log K_{ow} are available.

It is evident that with continued focus on passive sampling development and research that the technique will provide valuable information relevant to the future monitoring of our aquatic environment.

5.5 References

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